

**IDENTIFICATION OF SOURCES  
CONTRIBUTING TO THE CONTAMINATION  
OF THE GREAT WATERS BY TOXIC COMPOUNDS**

A report prepared for:

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## DISCLAIMER

This document was prepared by researchers in Great Waters-related scientific disciplines, and a draft of this report was reviewed by an expanded group of scientists at a workshop held in November 1992 in Chapel Hill, North Carolina. Other workshop participants included representatives from the U.S. Environmental Protection Agency, the National Oceanic and Atmospheric Administration, the International Joint Commission, and the affected States.

This report has been reviewed by the Office of Air Quality Planning and Standards, Pollutant Assessment Branch, U.S. Environmental Protection Agency, and has been approved for distribution as received from the team of authors. Approval does not signify that the contents reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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## EXECUTIVE SUMMARY

The Great Waters Program as written in section 112(m) of the Clean Air Act Amendments (CAAA) specifies that U.S. EPA, in co-operation with Commerce/NOAA, shall conduct a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants (HAPs) to the Great Waters which include the Great Lakes, Lake Champlain, Chesapeake Bay, and other coastal waters. In order to meet the ambitious goals set forth in the 1990 CAAA, EPA identified the need to determine the state-of-knowledge of atmospheric deposition of HAPs as a major pathway for loadings to the Great Waters.

This report evaluates the available data on the sources of HAPs within and outside the watersheds of the Great Waters (Great Lakes, Lake Champlain, and Chesapeake Bay), and discusses the difficulties in deriving such quantitative information. An effort is made to reconcile the emission data discussed with measured and estimated loading rates. Detailed inventories of the sources and emission intensities of HAPs has become an indispensable tool in environmental management. The quantitative targets are amenable to legislative controls, and the emission of the HAPs is easier to regulate than the resulting atmospheric deposition or food chain effects. Any attempt to set guidelines on deposition rates for HAPs, in fact, requires that the sources of the pollutants be known, and that emission rates be determinable.

Atmospheric deposition is one of the major sources of lead, arsenic, cadmium, mercury, PAHs, several organochlorine pesticides, (e.g., lindane, DDT, chlordane, dieldrin, toxaphene), PCBs, PCDDs, and PCDFs measured in the Great Waters. The other inputs include non-point sources, e.g., agriculture practices in the region, urban runoff, leaching from landfills, etc., direct industrial discharges, tributary inputs, and direct dumping of wastes. Specific examples of loadings estimates are given in the "Relative Loadings" section of the report. While approximately half of the lead is of atmospheric origin, it is noted that tributaries account for a substantial fraction as well. However, designating the loadings as being from tributary inputs maybe somewhat misleading as much of the lead and other contaminants in the tributary waters are the results of atmospheric deposition and subsequent runoff. There are many regions where high quality data are needed to fill-in the mass balance estimates for many HAPs. Even with the high-quality data in some areas it is very difficult to get a reasonable mass balance for a large majority of the critical pollutants.

Evidence of atmospheric deposition as a source of persistent semi-volatile organic compounds (SOCs) to water bodies is provided by their accumulation in soils, sediments, and

peat bogs in the Great Waters region and other locations. The trends of contaminant concentrations with depth in dated layers of sediments or peat cores track their known production/release history. These trends show peak accumulation of PAHs in the 1950s, PCBs in the mid-1970s, and organochlorine pesticides in the late 1960s to mid-1970s, depending on the chemical. Rapid increases of PCDDs/PCDFs in Great Lakes sediments after 1940 paralleled the production of chlorinated aromatic compounds, suggesting that incineration of chlorine-containing waste was the most significant contributor. Other indicators of atmospheric sources include direct measurements of SOC<sub>s</sub> in air, rain, and snow from the Great Waters and remote regions; and accumulation of persistent organochlorine compounds in biota from small inland lakes in the Northwest Territories, the high Arctic, and Antarctica.

Identifying the specific sources or source types emitting the pollutants into the atmosphere which ultimately are deposited is another matter. Identification of the major sources and the deposition pathways of the critical pollutants should be made for the individual compounds separately as their sources and behavior in the environment differ substantially. Volatile organic compounds (VOCs) and SOC<sub>s</sub> are emitted by both point and area sources. Examples of the former are stack and fugitive emissions from industrial processes and incinerators. Sources that emit pollutants over broad areas include vehicle exhaust and evaporation of pesticides and PCBs.

In general, both local and distant sources contribute to the pollution load at a given receptor. There are various definitions concerning the meaning of local and distant sources. In this work local sources are those in the states adjacent to the Great Waters. For the Great Lakes these states are Illinois, Indiana, Michigan, Minnesota, New York, Ohio, Pennsylvania, Wisconsin, and Ontario in Canada. For Lake Champlain the emission sources in the states of New York, Vermont and the Province of Quebec are considered local while local sources for the Chesapeake Bay are located in the states of Virginia and Maryland. Sources outside the above defined regions are regarded here as distant, regardless of how much they may contribute to the total loading of the Great Waters. This somewhat artificial division can be justified when considering various policy measures to reduce the pollution load. Local and distant sources can be of either anthropogenic or natural origin. It is believed that natural sources are more important when discussing the impact of distant source emissions on the atmospheric deposition of pollutants to the Great Waters.

Although a number of source-receptor techniques are available for estimating the contributions, it is still premature to conclude what part of pollution load originates within the study region and what part results from long range transport. The major reason for the present

uncertainty is the lack of reliable input data for application of these techniques including properly reported emission data. The present lack of monitoring data as well as emissions information is also problematic for other regions, e.g. the North Sea and the Baltic Sea, the two most extensively studied regions in Europe with respect to the environmental behavior of hazardous air pollutants.

In general, local sources are characterized on the basis of emission measurements and/or emission estimates. Representative measurements are considered the best information for accurately describing emissions. These measured data can be used for source characterization directly or indirectly. Direct use is when stack tests are performed using both continuous monitoring or representative grab sampling during short measurement campaigns. Measured data can also be utilized indirectly by transformation of the measurements into an emission factor or inclusion in a special calculation procedure.

Source characterization through measurements is often very expensive, and on some occasions extremely difficult to perform. In these cases other methods are often used, and in most circumstances are based on emission factors and /or mass balance calculations. The transparency and comparability of the data used to elaborate or select an emission factor from a handbook of emission factors are of great importance. The transparency of the data refers to the level of detail specified for the methods used to prepare a set of emissions factors, e.g., measurements of emissions rates or concentrations in exhaust gases together with the technological and meteorological conditions at the time that the measurements were obtained. Comparability of the data refers to emission factor verification/validation which includes comparison of the factors for a given source category obtained by various estimation methods.

Material or mass balance calculations can be applied to characterize emissions sources through the assessment of their emission quantities. The input quantities of the raw materials or fuel and the output rates of specific pollutants are determined. These rates are used to assess what fraction of a given pollutant is released in the gas phase while the balance is made for the amount of the pollutant associated with particles.

Emission sources can also be characterized using the concentrations of a given pollutant measured in ambient air at a receptor site. Measured concentrations are then compared with emission source profiles for major source categories likely to contribute to pollution at the site. This method, referred to as receptor modeling, is useful when emissions from a given source region originate from one dominant source or group of sources which have well defined emission profiles.

An important part of source characterization is to assess the accuracy of the methods used to prepare emission profiles and to verify source data. The accuracy of source characterization of emissions depends on whether the characterization has been made on the basis of actual measurements at the specific source or through estimation procedures. The methods based on measurements are considered as more accurate than those using assumptions and calculations, e.g., methods based on emission factors or material balances. Unfortunately, most verification procedures focus on activity data (statistical information) and emission factors.

Dispersion models have been the traditional work horse for calculating source-receptor relationships for air pollutants. These models require detailed emissions inventories for various sources for the pollutants of interest, e.g., SO<sub>2</sub>, NO<sub>x</sub>, etc. Even if the dispersion models were accurate it is very unlikely that the emissions inventories would be adequate. Emissions inventories for the criteria pollutants have many short-comings, as discussed earlier in this document, and these inadequacies are even more severe for HAPs or for pollutants which have large contributions from fugitive process emissions, natural sources, and dusts. The limitations of the dispersion oriented methods have led to the development of receptor models. Receptor models assess contributions from various sources based on observations at sampling or receptor sites.

Several methods are currently available to assess sources and source regions for various air pollutants based on the chemical composition of the air at a given receptor. Both the statistical methods and modeling are used together with meteorological data in order to obtain this assessment. The origin of the pollution measured at a given receptor can be studied using information on the chemical composition of aerosols and/or mixture of gaseous pollutants.

Statistical methods have been developed which use information on the chemical composition of aerosols to study contribution of sources or even source regions to the contamination at a given receptor. The applicability of multivariate techniques for resolving sources and source regions for aerosols measured at several locations remote from major emission regions has been tested using absolute principal component analysis (APCA) and the chemical mass balance (CMB) methods. APCA methods indicate the composition of major components, such as pollution, crust, and sea-salt components which contribute to the measured concentrations at receptors. In the past, the APCA methods were applied to air concentrations of total (both fine and coarse fractions) aerosols. Further improvement of this receptor modeling method was obtained by applying APCA to aerosol elemental concentration measurements in separate particle size fractions. The results of this application of APCA gives the basis for interpretation of



coupled chemical reactions and physical processes in remote locations, as well as giving information concerning atmospheric aging processes and, therefore, the history of the compounds.

Distinguishing sources through chemical mass balance (CMB) models and statistical methods (e.g., factor analysis, principal component analysis) is more problematic for organic compounds than metals. This is because VOCs and SOC<sub>s</sub> are transformed by chemical reactions in the atmosphere, and different rates of reactivity lead to changes in ratios among compounds during transport from source to receptor. In addition, some SOC<sub>s</sub> are associated to a greater extent with atmospheric particles than others. Preferential removal of particulate species by precipitation and dry deposition can alter the relative proportion of SOC<sub>s</sub> and other pollutants in ambient air. These changes are reflected in the chemical profiles of atmospheric deposition and sediments. For example, ambient air contains light and heavy PCBs, PCDDs, and PCDFs that are distributed between the vapor and particle phases. The heavier, more particle-bound compounds predominate in rain and sediments.

With a total VOC emission rate of 19.5 megatons (metric) per year, the United States leads the world in the release of most VOC types. Emissions are highest in the eastern third of the country. The relative contribution of various industries and vehicles to ambient air VOCs varies with location. Examples are presented in this report showing the use of CMB modeling and factor analysis to estimate the contribution of these point and area sources. The agreement between CMB results and emission inventories is encouraging in many cases.

Less work has been done with CMB and statistical methods for reconciliation of SOC sources. This is largely due to: a) difficulties in sampling and analytical techniques for SOC<sub>s</sub>, and b) alteration of chemical profiles by selective reactivity and physical removal of certain SOC<sub>s</sub>, as mentioned above. In a few cases CMB models have been applied to estimating the contribution of PAH sources in urban air. Principal component analysis has been used to distinguish patterns of PCDDs and PCDFs from different combustion sources in urban air, to examine changes in compound profiles that occur as a result of selective atmospheric deposition, and to differentiate PCDDs/PCDFs from combustion and pulp mills.

Several "marker" compounds have been proposed to help distinguish PAHs from different sources: wood combustion, spark vs. diesel engines, and unburned vs. burned petroleum products (combustion vs. street runoff). The main problem with these markers is that few are unique to a particular source type, and they are best applied in combination with other organic and inorganic tracers and with multivariate methods such as factor and principal component analysis.

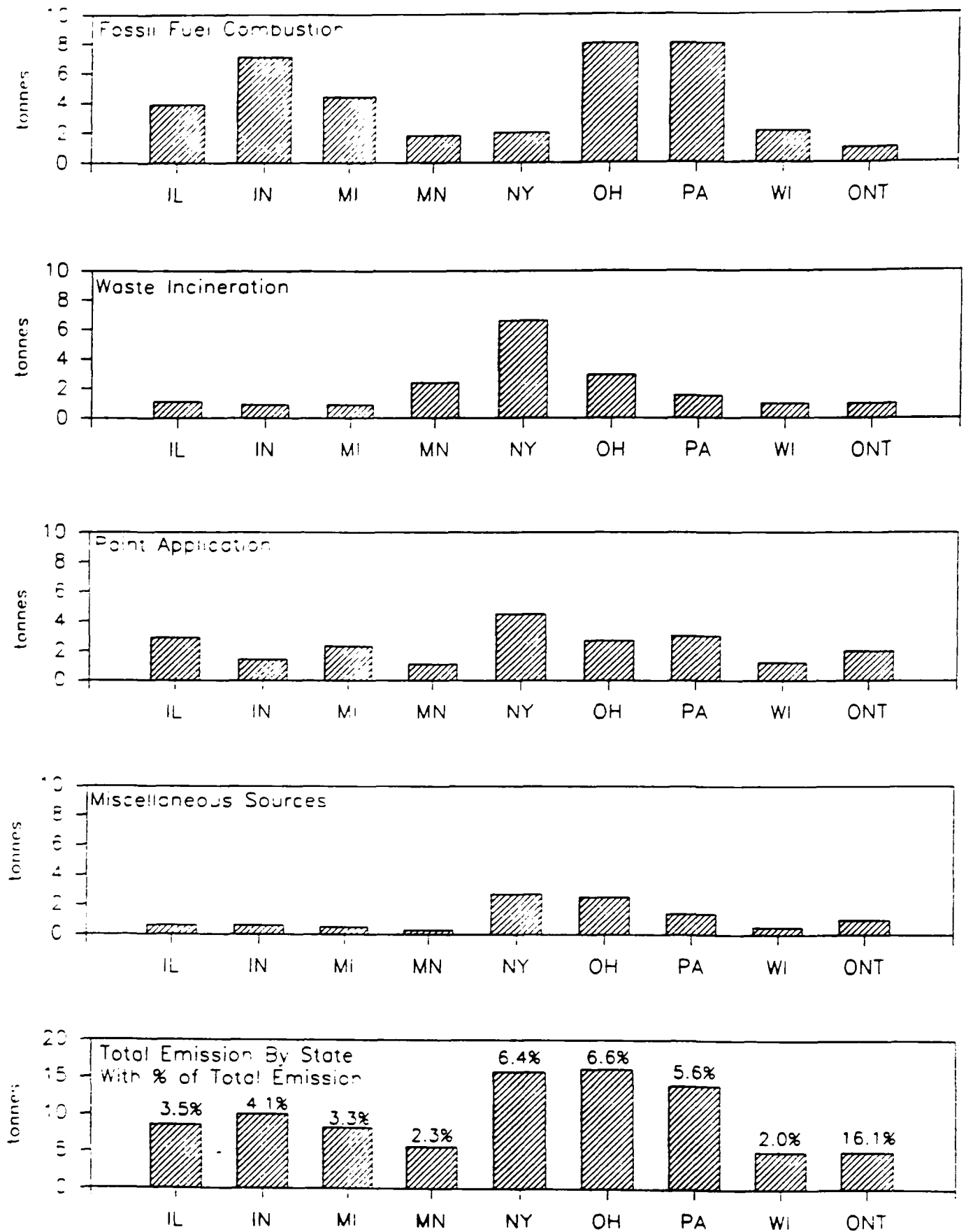
Identification of emission sources in the Great Waters regions and their characterization with respect to atmospheric emissions has been carried out for some time in both the United States and Canada. As a result, major source categories have been defined for all of the combustion-related HAPs, and include these sources: production of electricity and heat, combustion of fuels in industrial, commercial, and residential units, including wood combustion, manufacturing and use of various industrial goods, mobile source emissions, incineration of municipal and industrial wastes, and incineration of sewage sludge. **Figure 1** displays the mercury emissions from various source categories in the Great Lakes Basin. There are, however, differences in quantitative assessment of the fluxes from the above sources, reported by various research groups in the United States and Canada. These differences should be resolved through thorough examination of the available data using verification techniques for emission data and joint supplementary research programs in both countries.

A recent emissions inventory for Ontario and eastern North America has been prepared under contract for the Ontario Ministry of the Environment (MOE). Inventories for PAHs and PCDDs/PCDFs were derived after compilation of emission factors for a large number of source types, including industrial processes, vehicles, residential combustion (oil, gas, wood), power plants, incinerators, open burning, and forest fires. Estimated annual releases in eastern North America were 9397 metric tons PAHs and 414 kg PCDDs/PCDFs. The breakdown of PAH emissions by source type was: residential wood combustion 31%, other stationary fuel combustion (including power plants) 17%, industrial processes 29%, transportation 12%, other 11%. In the case of PCDDs/PCDFs, stationary fuel combustion and solid waste incineration each accounted for 46% of total releases.

The uncertainties in these estimates are major and difficult to quantify. This is largely due to the quality of emissions data, which are often incomplete and highly variable among sources, even within the same class. For example, reported emission factors for PCDDs/PCDFs from incinerators span more than an order of magnitude.

Emissions data currently reported by EPA and the IJC reveal that a large portion of the HAPs in the United States are generated outside the Great Lakes region. This is particularly true for emissions from point sources. The states neighboring the Great Lakes Basin, particularly Missouri, generate large quantities of these emissions in electricity and heat producing power

# Anthropogenic Sources of Mercury in the Great Lakes Basin



**Figure 1** Contribution of atmospheric emissions of mercury from various source categories to the state emissions in the Great Lakes region.

plants, primary and secondary non-ferrous smelters, steel and iron manufacturing plants, and waste incinerators. Sources in the St. Louis/Granite City area were found to be a major contributor to HAPs transported over Lake Michigan during a summertime pollution episode.

Emissions in regions outside the Great Lakes, Lake Champlain Basin, and the Chesapeake Bay, heavy metals and persistent organic compounds can and do reach the surface of these waters. While entering the atmosphere, these pollutants are subject to long range transport, transformations, and deposition processes "en route". The extent to which these processes occur depends on stack parameters, temperature and velocity of exhaust gases, meteorological conditions, and the physical and chemical forms of pollutants. Recent studies provide the basis for estimating what fraction of the HAPs emitted from major point sources is deposited in the vicinity of the emission sources (local deposition) and what part is transported and deposited outside the emission region.

Although PCBs are no longer sold in the United States and Canada, large reservoirs still remain. Of the 640,000 metric tons of PCBs produced in the U.S., 85% are estimated to remain in service (largely in transformers and capacitors), buried in landfills, and circulating in the environment. Releases of PCBs in eastern North America from leaking transformers and landfill gases were estimated at a few hundred kilograms per year. PCBs are also released during combustion, but emission factors for incineration of various types of waste are highly variable.

It has been difficult to obtain reliable figures for the production and use of pesticides in the United States and Canada because of proprietary restrictions which protect their release. However a recent survey has provided such information for herbicides on a state-by-state basis. Annual usage of the top ten herbicides in the U.S. totaled over 150,000 metric tons in 1987-89. Four chemicals -- atrazine, alachlor, metolachlor, and EPTC -- accounted for 62% of this total. The bulk of these pesticides (80% or more) were used on corn and soybeans. The National Oceanic and Atmospheric Administration (NOAA) reported application figures for 35 herbicides, insecticides, and fungicides in coastal drainage areas in the U.S., and provided details of use by crop and season. Use of the 35 chemicals in 1987 amounted to over 13,000 metric tons. Three estuarine drainage basins in the mid-Atlantic and southeast states ranked highest in pesticide use: Chesapeake Bay, Albemarle/Pamlico Sound, and Winyah Bay.

Organochlorine insecticides such as DDT, aldrin, endrin, dieldrin, chlordane, heptachlor, lindane, and toxaphene have been of most concern in the Great Waters because of their persistence and tendency to accumulate in biota. Most of these insecticides have been



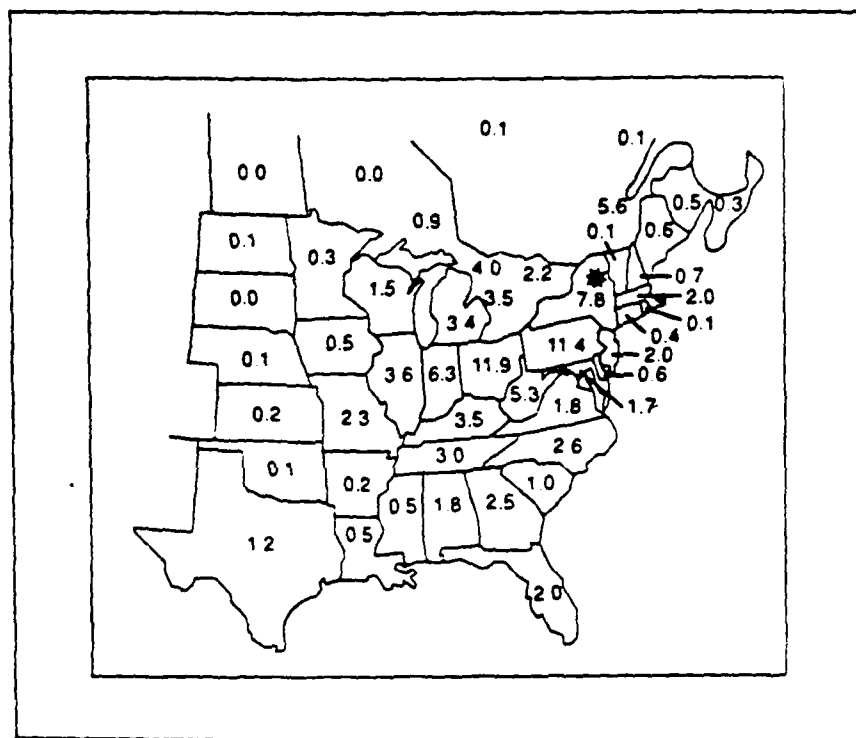
banned or severely restricted in the United States and Canada, but are still used in Mexico, Central and South America, Africa, and Asia. Reliable statistics on worldwide use that are needed to estimate the contribution of these foreign sources are largely unavailable.

In the case of emissions from point sources with a stack height of  $\geq 150$  meters (e.g. large power plants, primary non-ferrous smelters, cement kilns, steel and iron plants and waste incinerators), all of which employ high temperature processes, only 15 to 20 % of toxic emissions were deposited locally. The majority of the pollutants were transported out of the emission region. Research in the Great Waters Regions is needed to quantify local deposition. Particularly, information is needed on the importance of urban area emissions on deposition to nearby water bodies. It is certain that we must consider emission sources both within the Great Waters region and outside the watersheds in order to assess the origin of atmospheric toxic compounds deposited on the water surface in the region.

The quantity of emissions for the heavy metals and persistent organic compounds of concern in the states around the Great Lakes, Lake Champlain, and the Chesapeake Bay is difficult to assess due to diversity of emission numbers reported by various research groups. For most of the heavy metals considered in this work emission estimates differ by one order of magnitude and, therefore, are presently under revision.

Emissions from other source regions in North America may also affect the amount of pollution load deposited to the Great Waters although no definitive evidence has been provided by measurements and assessment for heavy metals and persistent organic pollutants. Compelling evidence suggests that pesticides applied in the southern portion of the U.S. are subsequently deposited into the Great Lakes and other bodies of water. Furthermore, the NAPAP concluded that such an impact exists for deposition of sulfate. The source receptor relationships calculated for wet sulfate deposition are shown in **Figure 2**. This figure suggests that the contribution from sources beyond 1000 km dominates the sulfate deposition to Lake Champlain and the Adirondack Mountain region. As the sulfates are transported on particles, as are many of the metals and organic compounds discussed in this report, one would hypothesize that the metals and organic compounds emitted from sources outside the study region would also be deposited to the Great Waters, especially those compounds that are emitted from the same sources as the sulfur. At present, regional models of long range transport of air pollutants are available and with some modifications they can be used to assess the contribution of emissions from outside source regions to the Great waters. An emission inventory with the appropriate spatial distribution of the data needs to be prepared. The experience gained through NAPAP emissions inventory development can be used as a starting point for this purpose. Collaboration with the Mexican authorities on

environment protection is highly recommended as the Mexican emissions of heavy metals and persistent organic pollutants are expected to contribute to the contamination of the Great Waters.



**Figure 2.** *Source apportionment of wet sulfate deposition (percent per state or subprovince) at Whiteface Mountain, NY*

Input of organochlorines to the Great Waters continues, as indicated by their presence in air and precipitation. Likely sources are long-range transport from countries where organochlorines are still applied, and volatilization from North American farmland treated years ago. Distinguishing "new" from "old" sources of these compounds is an essential and ongoing area of research. Tools for this purpose include air mass trajectories which can provide the history of the air mass on days with elevated levels of pesticides in the ambient air, often revealing a path from heavy use areas to the Great Waters, and examination of ratios among isomers and breakdown products of certain pesticides for clues to their source. Models have demonstrated that facile movement of organochlorine pesticides from the southern states to the Great Lakes can take place, and elevated concentrations of these compounds in Ontario air have been traced to air masses arriving from the south.

Evaporation rates of pesticides from treated fields have been measured and related to properties of the chemical, the soil, and the evaporation rate of water. The factors affecting pesticide volatilization are known, and models have been developed to predict fluxes from soils. There is a need to apply these measurement techniques and models to "old source" situations (fields treated in the past) and on a larger scale to obtain estimates of loadings to the atmosphere.

In the report to MOE, estimates of herbicide and insecticide releases to the atmosphere in eastern North America were 30,795 and 3,091 metric tons per year, respectively. These were based on usage information and a soil volatilization model. The insecticide figure is probably low, because it does not include a large number of current-use chemicals. At the present time it is not possible to attach a degree of uncertainty to these estimates, other than to say that it is probably large.

Gaseous SOCs, particularly PCBs and organochlorine pesticides, exchange freely between the atmosphere and the earth's surface -- water, soil, and vegetation. Seasonal high and low cycles of these compounds in ambient air are observed, which are correlated to temperature and thus volatilization rates. The Great Waters can act as either a sink or source of vapor-phase PCBs and pesticides, and gas exchange forms a large (and poorly understood) part of the contaminant budget. Long-range transport of persistent SOCs may not occur in a single event, but in steps as the compounds are continually deposited and revolatilized from land, water, and vegetation. Emissions from new sources must be cast in light of this global background of "recycled" material.

Pesticides, such as hexachlorocyclohexane (HCH), have been found to be global air pollutants measured in remote areas around the world. As the major application of this pesticide is in Asia and the wind patterns at various altitudes do not exclude the air mass transport from the Asian continent to North America, HCH deposited in the Great Waters regions may originate from as far away as India, China, or the former Soviet Union. This hypothesis can be tested by the application of global models, or at least hemispheric models. At present, such models are used to study the transport of green-house gases in the atmosphere and the transport of sulfur in the Northern Hemisphere.

Several methods can be applied to reduce emissions of toxic heavy metals and persistent organic pollutants and eventually reduce the atmospheric deposition of these pollutants to the Great Waters. Technological solutions presented in a form of Best Available Technology (BAT) package or Best Practicable Technology (BPT) package as well as non-conventional methods

offer emission reduction possibilities for point sources within all major source categories contributing to the contamination on the Great Waters. Previous experience gained in past efforts can be used in recommending emission reduction scenarios in the Great Waters region. Cost estimates and benefits from the implementation of the control techniques should be carefully studied.

New research initiatives are necessary in order to meet the requirements outlined in the conclusions of this report as well as to test the important hypotheses proposed here. These activities would include both measurement programs and modeling estimates.

Source inventories for combustion-related SOC's such as PAHs and PCDDs/PCDFs need to be improved. The wide variability in emission factors from various industrial and incineration processes will probably be reduced as emission controls are put into place.

Great improvements in sampling and analytical methods for SOC's have been made over the last decade, making the determination of source profiles more reliable. These improvements should lead to increased use of CMB models and statistical methods such as factor and principal component analysis for source reconciliation of SOC's. Additional "marker" compounds should be sought which can be used as source tracers.

Restrictions which protect the release of production and use statistics for pesticides in the United States and Canada must be removed to allow free exchange of this essential information. Further, an international effort is needed to identify types and quantities of pesticides used in foreign countries.

New measurement programs are needed in order to improve the quality of source-receptor techniques which are used to assess the magnitude and origin of deposited pollutants. These measurements are needed at both the receptor, the Great Waters themselves, as well as at the sources of the emissions. The following are recommended:

- emission rates and emission factors for toxic heavy metals and persistent organic pollutants from large point sources in the study region should be evaluated on the basis of measurements of their concentrations in exhaust gases;

- soil volatilization models for pesticides and mercury need to be improved and to the point where they can be applied regionally. These models should be validated by experimental measurements of pesticide and mercury fluxes from "old source" areas (previously treated land) as well as from freshly treated or contaminated fields and areas.



a program should be undertaken to identify and quantify current sources of banned organochlorine pesticides to the Great Waters. In particular, contributions from old sources within the U.S. and Canada should be assessed, and weighed against long-range transport of organochlorines from foreign countries.

new emissions of persistent SOC's must be evaluated relative to the global background of recycled material. To do this, we must determine the quantities of SOC's currently residing in the air, land, water, and vegetation reservoirs and the rates of exchange among these reservoirs.

- physical and chemical forms of the most volatile compounds should be established through measurements carried out in major sources in the study area; and
- emission rates for the most volatile metals, and particularly mercury, as well as SOC's should be derived on the basis of measurements over the water surface in the Great Waters and the surrounding soils. The results should be representative for the meteorological conditions as in the Great Waters and exemplify seasonal changes.

Measurements at receptors should provide information which is needed in order to improve the accuracy of source-receptor relationship analysis. The following is recommended:

- size-differentiated chemical composition of aerosols should be measured at receptors which can represent conditions over the water surface in the study area; and
- simultaneous measurements of the gaseous and particle phases of the studied pollutants with the help of newly developed techniques (e.g., denuder methods) should be undertaken in order to provide information on gas-to-particle conversions ( and particle-to-gas conversions) for the most volatile pollutants under study.

Improvement is needed within the three groups of estimates: emission estimates, dispersion modeling, and receptor modeling. The following is recommended for the improvement of emission estimates in order to assure better understanding of source identification in the Great waters region:

- gridded emission inventory for the studied pollutants should be approached for the whole territory of the United States and Canada;
- seasonal changes of mercury and volatile organic compound emissions need to be quantified and techniques developed to estimate these emissions; and
- an approach should be defined to assess emissions of pesticides in the Northern Hemisphere with particular emphasis on Mexico and the Asian countries.

Improvements in source identification through the further development of dispersion modeling for toxic air pollutants is needed. The following are recommended:

- continue to modify and improve the existing long-range transport models so they can be used to study the contribution of emissions from sources in North America, both within and outside the study region to the hazardous pollution load deposited to the Great Waters; and
- an approach should be made to apply the existing global scale models to investigate the possibility of pesticides, e g., lindane, used in Asia to be transported within air masses to North America and deposited also in the Great Waters region.

From the above discussion it is clear that there is a considerable amount of uncertainty in our estimates of the sources of the HAPS measured in the Great Water areas. The level of research activity must increase and cooperative programs must be implemented before our understanding of the sources of the critical pollutants found in the Great Waters will be complete enough for policy measures to be developed and implemented.

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## 1. INTRODUCTION

The Great Waters Program as written in section 112(m) of the Clean Air Act Amendments (CAAA) specifies that U.S. EPA, in co-operation with Commerce/NOAA, shall conduct a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants (HAPs) to the Great Waters which include the Great Lakes, Lake Champlain, Chesapeake Bay, and other coastal waters. In order to meet the ambitious goals set forth in the 1990 CAAA, EPA identified the need to determine the state-of-knowledge of atmospheric deposition of HAPs as a major pathway for loadings to the Great Waters.

Numerous reports document the fact that the atmosphere is a major source of toxic contaminants found in many aquatic ecosystems. This report includes an evaluation of the available data on the sources of HAPs within and outside the watersheds of the Great Waters (Great Lakes, Lake Champlain, and Chesapeake Bay), and will discuss the difficulties in deriving such quantitative information. Detailed emissions inventories of the criteria pollutants, e.g. SO<sub>2</sub>, NO<sub>2</sub>, etc, as well as HAPs have become an indispensable tool in environmental management. The quantitative targets are amenable to legislative controls and the emission of HAPs is easier to regulate than atmospheric deposition or food chain effects. Any attempt to set guidelines on deposition rates for HAPs, in fact, requires that the sources of the pollutants be known and the emission rates be determinable.

There is another cogent reason for concern about air emissions of toxics in this country. Of the 12 billion kilograms of the material flows reported in the Toxic Release Inventory (TRI) of 1988, about 39% (or 5 billion kg) went into the atmosphere, while only 6% and 9% were discharged directly to the surface waters and soils, respectively (EPA, 1990)<sup>1</sup>. In many aquatic ecosystems, however, large quantities of toxic contaminants can also be derived from industrial and municipal wastewater discharges, storm water and urban run-off, leachates from landfills and dump sites, etc. Furthermore, the transfer from one compartment to another becomes quite ambiguous as is in the case of combined storm-sewer systems in which contaminants are both directly discharged into the sewers as well as being deposited from the atmosphere with the precipitation. The wastewater eventually reaches a wastewater treatment plant which separates the liquids and solids, discharges the processed effluents into surface waters, and then often incinerates the solids removed in the process. The incineration of the sludge results in air

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<sup>1</sup> The quantity of toxic pollutants emitted is definitely underestimated in the TRI data as this inventory includes only 13% of the nations manufacturing facilities.



emissions which continues the cycle by dispersing the hazardous pollutants into the atmosphere where they are eventually deposited in a downwind environment by dry and wet processes. So, while the focus of this report is on air toxics, the need for an integrated or whole ecosystem approach to managing toxic contaminants in the Great Lakes should be emphasized.

## **2. ATMOSPHERIC DEPOSITION AS A MAJOR PATHWAY**

Atmospheric deposition is one of the major sources of lead, arsenic, cadmium, mercury, PAHs, several organochlorine pesticides, (e.g. lindane, DDT, chlordane, dieldrin, toxaphene), PCBs, PCDDs, and PCDFs measured in the Great Waters. The other inputs include non-point sources, e.g. agriculture practices in the region, urban runoff, leaching from landfills, etc., direct industrial discharges, tributary inputs, and direct dumping of wastes. Specific examples of loadings estimates are given in the "Relative Loadings" section of the report. While approximately half of the Pb is of atmospheric origin, it is noted that tributaries account for a substantial fraction as well. However, designating the loadings as being from tributary inputs maybe somewhat misleading as much of the Pb and other contaminants in the tributary waters are the results of atmospheric deposition and subsequent runoff. There are many areas where high quality data are needed to fill-in the mass balance estimates for many pollutants and it is very difficult to get reasonable numbers for a large majority of the critical pollutants.

Evidence of atmospheric deposition as a source of persistent semi-volatile organic compounds (SOCs) to water bodies is provided by their accumulation in soils, sediments, and peat bogs in the Great Waters region and other locations. The trends of contaminant concentrations with depth in dated layers of sediments or peat cores track their known production/release history. These trends show peak accumulation of PAHs in the 1950s, PCBs in the mid-1970s, and organochlorine pesticides in the late 1960s to mid-1970s, depending on the chemical. Rapid increases of PCDDs/PCDFs in Great Lakes sediments after 1940 paralleled the production of chlorinated aromatic compounds, suggesting that incineration of chlorine-containing waste was the most significant contributor. Other indicators of atmospheric sources include direct measurements of SOCs in air, rain, and snow from the Great Waters and remote regions; and accumulation of persistent organochlorine compounds in biota from small inland lakes in the Northwest Territories, the high Arctic, and Antarctica.

Compared to the other Great Waters considerably more research has been performed on the deposition of HAPs to the Great Lakes. Using the best "available" data quantitative estimates have recently been made on the fluxes of many toxic substances into these lakes (Eisenreich and Strachan, 1992). The relative importance of Great Waters contamination by atmospheric

deposition is the focus of another part of this report. However, the general conclusion can be drawn on the basis of a recent review (ICF, 1992 for EPA), that between 35 and 50% of the annual load of the HAPS of interest enter the Great Lakes waters through atmospheric deposition. It was concluded, for example, that the atmospheric lead input was responsible for 35 to 47% of all inputs to the Great Lakes during the period from 1977 to 1981.

The deposition of airborne toxic substances has also been studied in Europe. The results of long-term measurements on pollution of the North Sea and Baltic Sea waters lead to the conclusion that as much as 50% of lead and mercury and between 30 and 50% of arsenic, cadmium, chromium, copper, nickel, and zinc enter these waters through atmospheric deposition. The picture in Europe for the persistent organic compounds, discussed in this report, is very unclear due to lack of reliable measured data

The good agreement between the results obtained for the European Studies on the North Sea and the Baltic Sea, and the findings reported for the Great Lakes indicates that atmospheric deposition is a very important pathway for HAPs measured in these waters. This indication, although regarded as preliminary, due to limited data for most of the organic toxins, argues for research on sources and source regions generating atmospheric emissions of the studied pollutants to identify the major sources of the Great Water's contamination. Once identified, the major sources (often called "hot spots") can be targeted and emissions reduction programs can be implemented leading to a decrease in the pollution load to the Great Waters.

Identifying the specific sources or source types emitting the pollutants into the atmosphere which ultimately are deposited is another matter. Identification of the major sources and the deposition pathways of the critical pollutants should be made for the individual compounds separately as their sources and behavior in the environment differ substantially. Volatile organic compounds (VOCs) and SOCs are emitted by both point and area sources. Examples of the former are stack and fugitive emissions from industrial processes and incinerators. Sources that emit pollutants over broad areas include vehicle exhaust and evaporation of pesticides and PCBs.

In general, both local and distant sources contribute to the pollution load at a given receptor. There are various definitions concerning the meaning of local and distant sources. In this work local sources are those in the states adjacent to the Great Waters. For the Great Lakes these states are Illinois, Indiana, Michigan, Minnesota, New York, Ohio, Pennsylvania, Wisconsin, and Ontario in Canada. For Lake Champlain the emission sources in states of New York, Vermont and the Province of Quebec are considered as local while for the Chesapeake Bay,

the states of Virginia and Maryland. Sources outside the above defined region are regarded here as distant, regardless of how much they may contribute to the total loading of the Great Waters. This somewhat artificial division can be justified when introducing various policy measures to reduce the pollution load. Local and distant sources can be of either anthropogenic or natural origin. It is believed that natural sources are more important when discussing the impact of distant source emissions on the atmospheric deposition of pollutants to the Great Waters.

Although a number of source-receptor techniques are available for estimating the contributions, it is still premature to conclude what part of pollution load originates within the study region and what part results from long range transport within air masses. The major reason for the present uncertainty is the lack of reliable input data for application of these techniques including properly reported emission data. The present lack of monitoring and emissions data is also problematic for other water bodies currently being studied with respect to the environmental behavior of hazardous air pollutants, e.g. the North Sea and the Baltic Sea.

### **3. GENERAL PROCEDURES FOR SOURCE IDENTIFICATION**

There are a number of methods which can be used to identify sources or source regions contributing to the pollution load measured at a given receptor. These can be categorized into statistical methods, chemical and isotopic trace methods, meteorological methods including trajectory techniques, and various combinations of these approaches. Emissions of the compounds discussed in this report to the atmosphere are multitudinous. Most of the compound classes discussed here stem from human activities, although natural sources make a contribution in some cases. For example, PAHs are released both by anthropogenic combustion and forest fires and Hg is emitted during coal combustion and is released from mines and soils. Source characterization, when performed accurately, is a powerful tool for the assessment of emissions from local sources. To assess atmospheric deposition to a receptor such as the Great Waters and recommend remedial action, it is necessary to know the relative contribution of various sources to the total mass loading. These are deduced from a combination of source characterization and source apportionment techniques such as emissions inventories, dispersion modeling, multi-variate (statistical) methods such as factor analysis, and chemical mass balance (CMB) models. Some of these methods are briefly described by Zweidinger *et al.* (1990), and Sweet and Vermette (1992) in their article on VOCs in Illinois and St. Louis, and expanded upon in their references, and in Gordon (1988), Henry *et al.* (1990) and Hopke (1991).

Source apportionment methods, often referred to as receptor models are based on statistical techniques using measurements and information on sources for an assessment of the

local source contributions. These techniques used together with meteorological information can also be utilized for assessing the contributions of distant sources. Receptor models that implicitly incorporate meteorological data are often referred to as hybrid models (Keeler, 1987).

### 3.1. Source characterization

In general, local sources are characterized on the basis of emission measurements and/or emission estimates. Representative measurements are considered the best source of information for accurately describing emissions. Measured data can be used for source characterization directly or indirectly. Direct use is when stack tests are performed using both continuous monitoring or representative grab sampling during short measurement campaigns. Examples of inventories developed for semi-volatile organic compounds (SOCs) are given in Johnson *et al.* (1992). There are several regulations in force requesting measurements of emissions rather than estimation for certain types of sources or source categories, e.g. the Commission of European Communities requests emission measurements for power plants with capacity higher than 300 MW. In the U.S., the TRI program also requests any industry with 10 or more employees to report the release of any of the 322 compounds on the TRI list.

Indirect use of measured data for source characterization is whenever information obtained from measurements is transformed to an emission factor or included in a special calculation procedures. Emission factors for PAHs in mass/vehicle-km are developed from auto exhaust sampling or measurements in traffic tunnels. Sampling in stacks yields emission factors for industries, power plants, and incinerators. Often these can be related to fuel usage; e.g. mg PAHs released per ton coal burned. Aerial pesticide losses are estimated from models relating spray drift and volatilization to application rates, soil properties, and meteorological factors. Emissions are usually apportioned to a grid network for dispersion modeling and impact assessment.

Source characterization through measurements is often very expensive, however, and on some occasions extremely difficult to perform. In these cases other methods are often used, and in most circumstances methods based on emission factors and /or mass balance calculations are employed. The transparency and comparability of the data used to elaborate or select an emission factor from a handbook of emission factors are of great importance.

Mass balance calculations can be applied to characterize emission sources through the assessment of their emission quantities. The input and output rates of a given pollutant are determined and are used to assess what portion of a given pollutant is released in the gas phase

while the whole balance is made for the amounts of the pollutant on particles. For example, to calculate the mercury mass balance for the combustion of coal, the amount of the mercury in the coal is compared to the amounts of mercury in the fly ash, bottom ash, and stack dust. The imbalance is explained as the amount of mercury leaving the stack in the gas phase.

Emission sources can also be characterized using the concentrations of a given pollutant measured in ambient air at a receptor site. Measured concentrations are then compared with emission source profiles for major source categories likely to contribute to pollution at the site. It is clear that this method is useful when emissions from a given source region originate from one dominant source or group of sources which have well defined emission profiles. A large electric power plant in a region with small industry can be a good example of such a case. In the case of complex source region more statistical work is needed to specify the contribution of various sources to a profile which can be then compared with a profile obtained from ambient measurements. Principal component analysis (PCA) is often used in such case, where the contributions from several sources can be de-coupled in the ambient data. PCA has been used to define source profiles in cases where there are no source profiles available from source sampling (Tuncel *et al.*, 1985).

An important part of source characterization is to assess how accurate are the methods used to prepare source profiles are and what are the means of verification of source data. Accuracy of source characterization in terms of emissions depends on whether the characterization has been made on the basis of measurements or estimates. The methods based on measurements are considered as more accurate than those using assumptions and calculations, e.g. methods based on emission factors or chemical mass balances. Unfortunately, most of the verification procedures focus on activity data (statistical information) and emission factors.

### **3.2. Source apportionment techniques**

Historically, dispersion models have been the traditional work horse for calculating source-receptor relationships for air pollutants. These models require detailed emissions inventories for various sources for the pollutants of interest, e.g. TSP, SO<sub>2</sub>, etc. Even if the dispersion models were accurate it is very unlikely the source emissions inventories for the pollutants of interest would be adequate. Emissions inventories for the criteria pollutants have many short-comings, as discussed earlier in this document, and these inadequacies are even more severe for hazardous pollutants or for pollutants which have large contributions from fugitive process emissions, natural sources, and dusts. The limitations of the dispersion oriented methods have led to the development of receptor oriented models. Receptor models assess contributions

from various sources based on observations at sampling or receptor sites. Gordon (1980, 1888) reviews the development of receptor methods and provides a concise overview of the various types of receptor models and their applications. Here, we will briefly describe a few of these techniques and discuss how they can be applied along with dispersion models to define source-receptor relationships for hazardous air pollutants.

Receptor models were developed in the early 1970s in an attempt to identify the source(s) of particulate matter in large urban areas and to quantify the amount of particulate matter emitted from the source(s) (Miller *et al.*, 1972; Gordon, 1980; Winchester and Nifong, 1971). The chemical element balance, or chemical mass balance (CMB) method as it is now referred, are based upon the premise that the emissions characteristics, in terms of chemical and elemental composition as well as physical size and morphology, of various source types are different enough that one can identify their contributions by measuring the characteristics in samples collected at a receptor site. Thus, an important first step in the application of CMB model to apportion the sources of air pollutants measured in a specific urban area is to define an emissions inventory of the number and source types of the important sources of air pollution. These models assume that the composition of all contributing source types are known. This is often not the case either because the sources are not easily sampled or because the source classes have widely varying compositions (Henry, 1991). This is an important limitation of the CMB method in that the lack of specific source profile information for the pollutants of interest prevent this approach from being applied. Emissions data have been sparse in the past, particularly for SOCs, but the situation is improving.

While the CMB method has primarily applied to urban scale data, Rahn and Lowenthal (1984, 1985) also applied this technique to their "regional signatures" to apportion the sulfate and trace metals observed on particulate. The application of receptor models to regional and global scale problems has been controversial and has yet to be developed, in some peoples opinions, to the level necessary for it to be thought of as definitive in nature. However, an independent verification for the appropriateness of the trace element ratio approach was performed and indicated that this technique can be quite powerful (Keeler, 1987; Keeler and Samson, 1989).

Several methods are currently available to assess sources and source regions for various air pollutants on the basis of the data on the chemical composition of the air at a given receptor. Both the statistical methods and modeling are used together with meteorological data in order to obtain this assessment. The origin to the pollution measured at a given receptor can be studied using information on the chemical composition of aerosols and/or mixture of gaseous pollutants.

### 3.3 Applications of source apportionment techniques for metals

Statistical methods have been developed which use information on the chemical composition of aerosols to study contribution of sources or even source regions to the contamination at a given receptor. The applicability of multivariate techniques for resolving sources and source regions for aerosols measured at several remote locations far from major emission regions has been tested with the use of the absolute principal component analysis (APCA) and the chemical mass balance (CMB) methods. The APCA method determines the composition of the major source components, such as coal combustion related, crustal, or sea-salt related which contributed to the measured concentrations at the receptors. In the past, the APCA method was applied to total suspended particulate concentrations (particles measured in both the fine and coarse fractions). APCA has been utilized to study the origin of the Arctic aerosol. The results of these studies can be summarized as follows. The anthropogenic component contained many toxic compounds, however, some crustal material was also found with this component. A second component containing the crustal elements was observed with proportions similar to those found in the average crustal rock. However, most of the elements in the soil component were highly enriched and this fact suggests that the second component also contained some material from anthropogenic sources. The composition of the third component found in the Arctic aerosol was fairly similar to that of bulk seawater, indicating that this component is essentially sea-salt. The three-component solution for the Arctic winter aerosol was confirmed by several studies (Barrie *et al.*, 1992).

Further improvement of this receptor modeling method was obtained by applying APCA to aerosol elemental concentration measurements in separate particle size fractions (e.g. Li and Winchester, 1990). The results of this application of APCA gives the basis for interpretation of coupled chemical reactions and physical processes in remote locations, as well as giving information concerning atmospheric aging processes and, therefore, the history of the aerosols. For example, it was noticed that some crustal particle components were found in all size fractions. Carbonaceous fuel combustion pollutants were indicated by the presence of Si and Cl and the absence of Al in all size fractions, and they were usually rich in sulfur. The combustion of coal with high ash content may release volatile SiO from reduction of silicon dioxide by carbon, which then forms a fine aerosol after SiO oxidation back to silicon dioxide. Since Al is non-volatile during coal combustion its absence when Si and other metals were present indicates the aerosol was generated from burning high ash content coal.

Principal component analysis (PCA) has also been applied to assess the origin of the remote aerosols on the basis of results from automated microanalysis of individual particles. For example, Anderson *et al.* (1992) employed a modified scanning electron microscope (SEM) analysis of particles to study the origin of the Arctic aerosol. They concluded that the collected aerosol contained a mixture of altered and unaltered particles types from a variety of sources, such as coal combustion, sea salt, and crustal dust. The silicate types appeared as relatively unaltered particles, as well as particles with sulfate coatings, and also as particles that have reacted with Br. Most silicate particles are probably crustal in origin. Many compositional types of metal-rich particles were of anthropogenic origin, and most types had temporal variation patterns that are individually distinct. Other major particle types were of marine origin, but extensive fractionation and reactions of the marine aerosol components was suggested. The authors concluded that further research is needed on the nature and timing of these reactions, the mechanism for fractionation of the marine aerosol, and the sources of some particle types. It was also underlined that the complexity of the remote aerosols during a period presumed to be relatively free of pollutants is striking. Two important findings were that (1) the Arctic aerosol has pollution products from human activity even in a normal period of spring; and (2) many of the apparent pollutant particles in the fine fraction, S-rich species and perhaps Br-rich species, are of natural origins.

Single or Individual Particle Analysis (IPA) has been applied in aerosol research to investigate the sources and morphology of the collected atmospheric particulate matter (Dzubay and Mamane, 1989; Mamane, 1990; Sheridan, 1989). In the review by Sheridan (1989) he observed that particles emitted by anthropogenic sources, such as carbon soot and coal combustion spheres, occurred simultaneously with the highest concentrations of H<sub>2</sub>SO<sub>4</sub> droplets. Mamane (1990) utilized scanning electron microscopy (SEM) to estimate the contribution of refuse incinerators to Philadelphia. Thus, IPA can be used to estimate the source apportionment but also physical and chemical processes occurring during the long range transport of air pollutants. Single particle analysis provides critical size distribution information that can be directly used to calculate the deposition of pollutants as a function of size.

One important limitation of the PCA methods is, however, that their results do not allow one to obtain a fine resolution of the contributions from various distant source regions to the chemical composition of the remote aerosol. To attempt this resolution, CMB source apportionment must be performed using either a set of emission source profiles or a set of elemental signatures. The emission source profiles will be discussed later in this report. One set of elemental signatures were developed by Rahn and Lowenthal (e.g. Lowenthal and Rahn, 1985).



The CMB source apportionment proved to be a good technique to assess contributions from major source regions but was often limited to provide fine resolution of the contributions from more defined areas due to high collinearity of signatures or source profiles used. For example, the use of three European signatures in the Rahn and Lowenthal studies was supposed to provide a fine resolution of the contributions from various parts of Europe to the contamination of the Arctic aerosol. This attempt failed due to high collinearity of the European signatures. Therefore, both the PCA and CMB methods are with limitations when comes to fine resolutions of emission source regions contributing to the remote aerosol.

The origins of aerosols in remote regions and their source apportionment have been diagnosed with the help of not only heavy metals but also of isotopes, halogens, graphitic carbon, and organic compounds. Stable lead isotope ratios have been used to assess the contribution of emissions from various source categories, anthropogenic vs. natural sources, or to distinguish various sources within the same source category, e.g. combustion of gasoline with lead additives from various manufacturing plants, to the lead concentration or atmospheric deposition at a given receptor (Sturges and Barrie, 1989; Graney *et al.*, 1992). The ratios between the lead isotopes in aerosols in the United States and Western Canada were found to be much higher than those in the Arctic aerosol, while for Europe they were lower. The ratios in Eastern Canada were similar to the Arctic data, but meteorology argues against this region being a major contributor to the Arctic air pollution. The stable isotope analysis was taken a step further by Graney and colleagues in that they linked sediments from three Great Lakes to air concentrations in the basin to ascertain the extent of regional anthropogenic lead pollution, and to investigate the extent to which the sediment cores could be used as indicators of historical atmospheric deposition. One limitation of the above described method is that it requires a detailed information on the isotope ratios at emission sources, which is not always available. In addition, the isotope ratios at emission sources are often not sufficiently different to permit the use of multivariate statistical models to resolve the input ratios.

Concentrations of chlorine, bromine, and iodine have been used to assess the contribution of emissions from marine, automotive, and crustal sources to the contamination of the air at a given receptor. Other sources, such as coal combustion have been also identified using the halogen concentrations and their ratios. However, an important limitation of this method is that halogens are quite reactive in the polluted troposphere and their behavior during long range transport may be affected by the chemistry of the atmosphere. Therefore, the application of halogens as source tracers is probably limited to pristine regions, such as the Arctic rather than in the polluted regions, such as the Great Waters area.

High concentrations of graphitic carbon particles have been used to estimate the contribution of combustion emissions at several receptors (e.g. Rosen and Hansen, 1984). Further work on this subject has been focused on assessing the vertical distribution of graphitic carbon particles and their associated absorption coefficients. Although this research is very important for modeling the effects of air contamination on the solar radiation balance, it seems to be less useful in assessing the origin of pollutants at receptors.

A number of receptor-oriented transport models have been developed to identify the emission source regions contributing to the contamination of certain areas by trace metals. In general, the models have proven useful in calculating trace element concentrations at various remote receptors and trace element inputs. A Lagrangian-type of model was employed to determine the origin of air pollutants measured during the transport episodes to the Arctic (e.g. Pacyna *et al.*, 1985) as well as to the remote locations in Scandinavia (e.g. Pacyna *et al.*, 1989). It was concluded that concentrations calculated by models agreed with measurements within a factor of two. Of course, the model results depend on the quality of emission inventories used as an input data. The model performance is also sensitive to the dry and wet deposition processes. Fixed values of the dry deposition velocities are often used in models. This is certainly a simplification of the problem raising the inaccuracy of the modeling. The mixing height also affects the performance of the model, but far less than the emission estimates and the wet and dry deposition processes.

The variational formulation of Eulerian dispersion models also allows for the application of both source-oriented and receptor-oriented modeling as complementary tools in identification of sources contributing to the contamination of the environment in a given region. Uliasz and Pielke (1990) concluded that applicability of the receptor oriented option is limited to linear dispersion models and integrals describing air quality at the receptor. It is necessary to assume that all chemical reactions of pollutants are linear and that pollutants do not affect the atmospheric dynamics. Uliasz and Pielke (1990) suggest, however, that their variational approach may be still useful to perform sensitivity analysis of dispersion models with nonlinear chemistry.

An improved climatological-type model on Trace Toxic Air Concentrations in Europe (TRACE) has been developed by Alcamo *et al.* (1993). The model addresses some of the drawbacks to typical climatological-type air pollution models by (1) computing time of travel from an empirical function of geographic distance; (2) maintaining mass conservation by splitting the computation of decay coefficients spatially, and deriving concentration equations from mass considerations, (3) dividing calculations into two steps and calculating deposition based on local meteorological variables, thereby avoiding unreasonably "smooth" spatial deposition patterns; and

(4) deriving all parameters objectively, that is, without calibration to observations. TRACE has been used to compute levels of heavy metals for 1978 to 1985 throughout Europe. Calculations agreed with As and Pb observations within a factor of two, and underestimated Cd and Zn observations. Using the model it was estimated that wet deposition exceeds dry deposition in most of Central Europe. The mean residence time of the mass of heavy metals in Europe's lower atmosphere was estimated between 64 and 96 hours.

### **3.4 Problems in the application of source apportionment techniques for organic compounds: changes in chemical profiles from source to receptor**

It might seem that if source chemical profiles were known, the same apportionment could be applied to atmospheric deposition. However the problem is much more complex. Because of their reactivity and exchange between different phases in the atmosphere (gas-to-particle distribution) organic compounds behave less conservatively than elemental tracers. Thus, changes in the relative abundance of individual compounds occur in transit from source to receptor due to differential reactivity and rates of atmospheric deposition. The limitations imposed by alteration of profiles are not well understood. This section gives an overview of factors responsible for profile changes; problems with individual compounds or compound classes are dealt with in the appropriate section.

Gaseous and particulate organic compounds can be transformed by photolysis, and are also more or less reactive toward a number of atmospheric species, including radicals (e.g. hydroxyl, peroxy), ozone, and nitrogen oxides (Atkinson, 1990; Ballschmiter, 1991; Bunce and Nakai, 1989; Bunce *et al.*, 1989). Differential reactivity is a factor which limits source identifications based on chemical profiles obtained at a distance. Calculated atmospheric lifetimes for gas-phase reactions of several VOCs and SOCs with OH radicals range from a few hours to nearly half a year (Table 1), and thus ratios of compounds change in traveling from source to receptor. Scheff and Wadden (1991) considered the effect of reactivity on CMB models for VOCs and concluded that for most species a 2-3 hour transit time from source to receptor would result in little change in composition ratios. Nevertheless, diurnal cycles of several gaseous 2- and 3-ring PAHs were observed in Glendora, California during a photochemical air pollution episode (Arey *et al.*, 1989). Daytime concentrations were about 2-3 times lower than at night due to reaction with the higher levels of OH radicals during the day. Elevated nighttime concentrations of nitronaphthalenes were found as a consequence of naphthalene reaction with  $N_2O_5$ . Transformation of particulate PAHs may also be a problem, and is discussed in that section.

**TABLE 1.** Estimated Atmospheric Lifetimes Due to Gas-Phase Reaction with OH Radicals.

<u>Compound</u>	<u>Lifetime</u>	<u>Compound</u>	<u>Lifetime</u>
<b>Aliphatics</b>		<b>PCBs</b>	
Alkanes, C <sub>4</sub> - C <sub>13</sub>	0.5 - 6 days	Monochloro	5-11 days
		Dichloro	8-17 days
<b>Aromatics</b>		Trichloro	14-30 days
		Tetrachloro	25-60 days
Benzene	5 - 13 days	Pentachloro	60-120 days
Toluene	1 - 2.5 days		
Xylenes	6 - 10 hours	<b>PCDDs &amp; PCDFs</b>	
Trimethylbenzenes	4 hours	2,3,7,8-TCDD	2-3 days
Ethylbenzene	20 hours	2,3,7,8-TCDF	7 days
Ethyltoluenes	7 - 11 hours		
Naphthalene	8 hours		
Biphenyl	2 - 3 days		
Fluorene	1.2 days		
Anthracene	1.4 hours		
Pyrene	4 hours		
		<b>Pesticides</b>	
<b>Chlorinated VOCs</b>		DDT, DDE	2-4 days
		Dieldrin	1 day
Methyl chloride	1 year	Chlordane	8 days
Dichloromethane	110 days	Hexachlorobenzene	80 days
Chloroform	150 days	Hexachlorocyclo-	
1,2-Dichloroethene	70 days	hexane	15 days
Trichloroethene	6 days	EPTC	5.8 hours
Tetrachloroethene	90 days	Cycloate	5.2 hours

Sources: Altschuller *et al.*, 1991; Atkinson (1987), Bidleman *et al.* (1990); Kwok *et al.* (1992).

SOCs differ from VOCs in that they are associated to a greater or lesser extent with atmospheric particles. This phase distribution profoundly affects their atmospheric chemistry and physical removal, and thus deposition into the Great Waters (Ballschmiter, 1991; Bidleman, 1988; Mackay *et al.*, 1986; Schroeder and Lane, 1988; Swackhamer and Eisenreich, 1991). Factors influencing the extent of particle association include compound volatility (vapor pressure), temperature, and particle surface area available for adsorption. The Junge-Pankow equation (Pankow, 1987) is the most common model for estimating the phase distribution of SOC in ambient air:

$$\Phi = c\Theta / (p_L^0 + c\Theta) \quad (1)$$

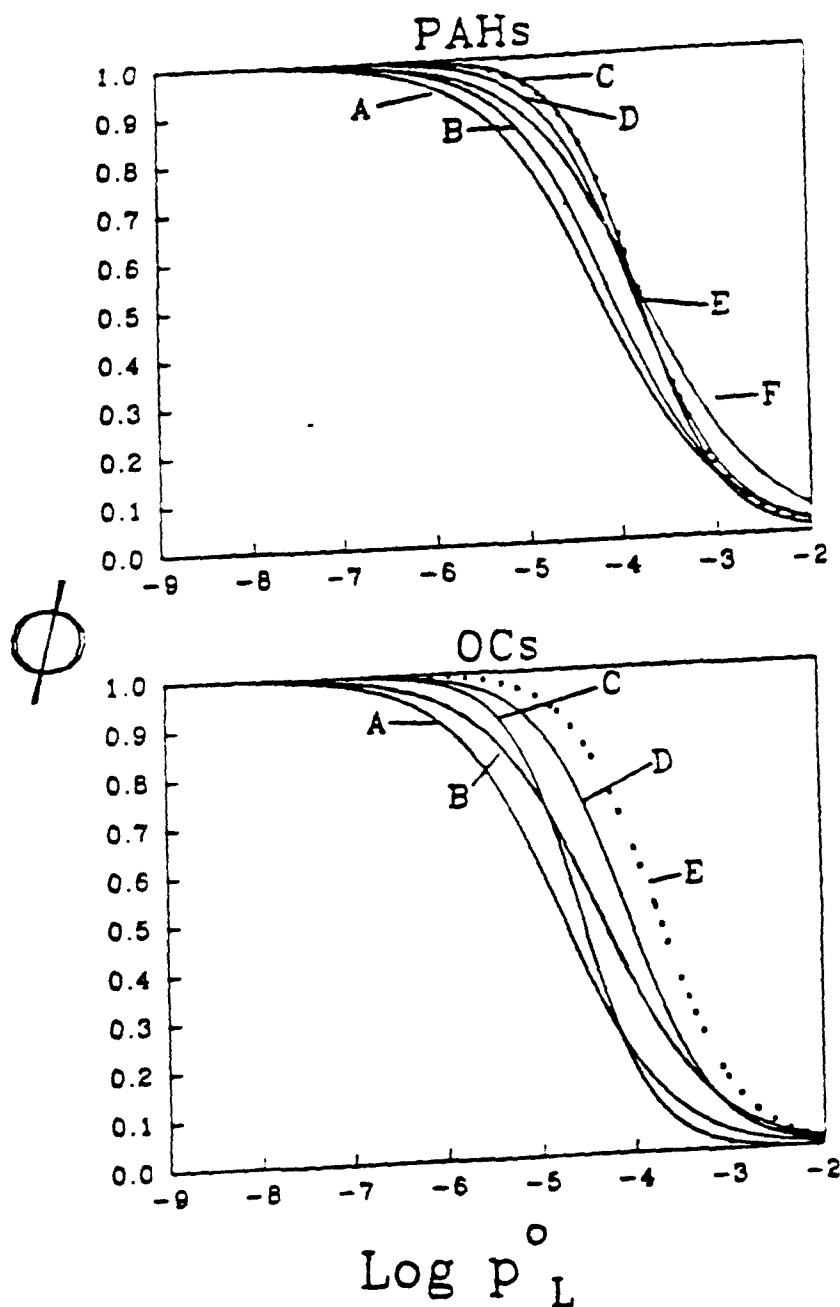
In Equation 1,  $\Phi$  is the fraction of the total atmospheric concentration associated with aerosols,  $p_L^0$  is the liquid-phase vapor pressure of the compound, and  $c$  is a parameter which depends on thermodynamic properties of the compound and surface properties of the aerosol. The parameter  $\Theta$  is the available particle surface area per unit volume of air ( $\text{cm}^2/\text{cm}^3$ ); typical values for urban, rural, and clean background air are given by Bidleman (1988).

Experimental estimates of the phase distribution of SOC in air are usually made by drawing air through a filter to retain particles followed by an adsorbent trap to collect gaseous SOC. Such samplers are prone to a number of artifacts which may cause the measured

particulate fraction on filters to differ from the phase distribution in the free atmosphere (Pankow and Bidleman, 1992). Evaluation of these artifacts (Cotham and Bidleman, 1992; deRaaij *et al.*, 1990; McDow and Huntzicker, 1990; Zhang and McMurray, 1991) and development of improved techniques to speciate SOC (e.g. denuder samplers, Appel *et al.*, 1989; Coutant *et al.*, 1992, 1989; Krieger and Hites, 1992; Lane *et al.*, 1988) is an active area of research.

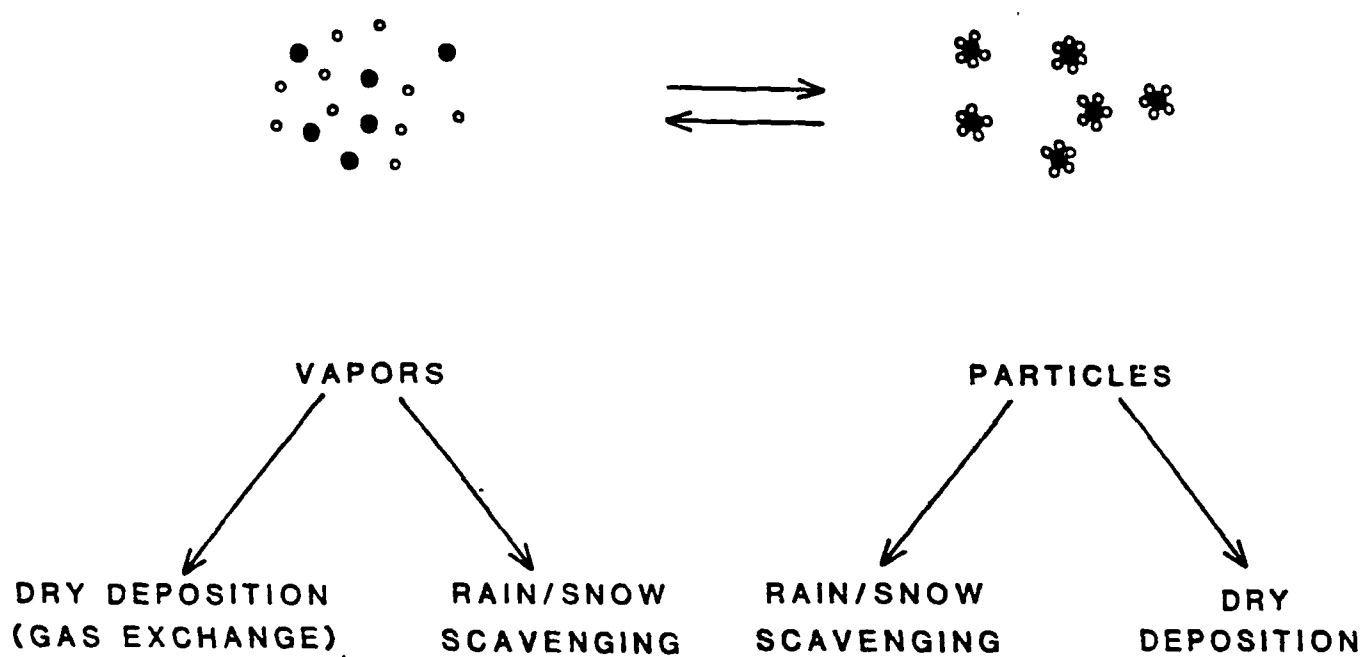
Particulate fractions measured with filter-adsorbent samplers and predicted by the Junge-Pankow model have been made in a few cities and rural areas. These comparisons, summarized by Bidleman (1991), and Pankow and Bidleman (1992) show good agreement between the model and experimental results for PAHs, whereas the sampling methods yield  $\Phi$ -values that are lower by about a factor or two for organochlorine pesticides, PCBs, PCDDs, and PCDFs (Figure 1).

The gas-to-particle distribution of SOC governs the mechanism and rate of their removal from the atmosphere. Deposition of SOC can occur by wet and dry removal of particles, and gas exchange with soil, plant foliage, and water bodies (Figure 2). An understanding of gas-particle relationships in the atmosphere is therefore necessary to predict losses of SOC during transport



**Figure 1.** Particulate percentages of PAHs and organochlorines (PCBs, pesticides, PCDDFs) in urban air, as determined by high volume air sampling (solid curves) and predicted by the Junge-Pankow model (Equation 1) as a function of the liquid-phase vapor pressure ( $p_L^o$ , Pa) of the chemical. Letters indicate individual investigations. Source: Cotham (1990) and Bidleman (1991).

## AERIAL DISTRIBUTION AND REMOVAL OF SOC



**Figure 2.** Gas-particle partitioning and aerial removal processes for SOC. Source: Bidleman (1988, 1991).

and deposition. An equilibrium model describing the relationship between wet scavenging and the fraction of particle-bound SOC is (Ligocki and Pankow, 1985):

$$W = W_p\Phi + W_g(1-\Phi) \quad (2)$$

$W$  is the overall scavenging ratio (concentration in rain divided by concentration in air, on a volume-volume basis),  $W_p$  and  $W_g$  are scavenging ratios for particulate and gaseous SOC.  $W_p$  is obtained from field observations for species only in the particulate phase (such as certain trace metals).  $W_g$  is the equilibrium water/air partition coefficient, calculated from  $RT/H$  where  $H$  is the Henry's law constant ( $\text{Pa}\cdot\text{m}^3/\text{mol}$ ) for the particular species and  $R$  is the gas constant ( $8.3 \text{ Pa}\cdot\text{m}^3/\text{deg}\cdot\text{mol}$ ). Thus the relative importance of particle and gas scavenging for an individual compound depends on its phase distribution ( $\Phi$ ) and the Henry's law constant. These must be known as a function of temperature to estimate atmospheric removal rates.

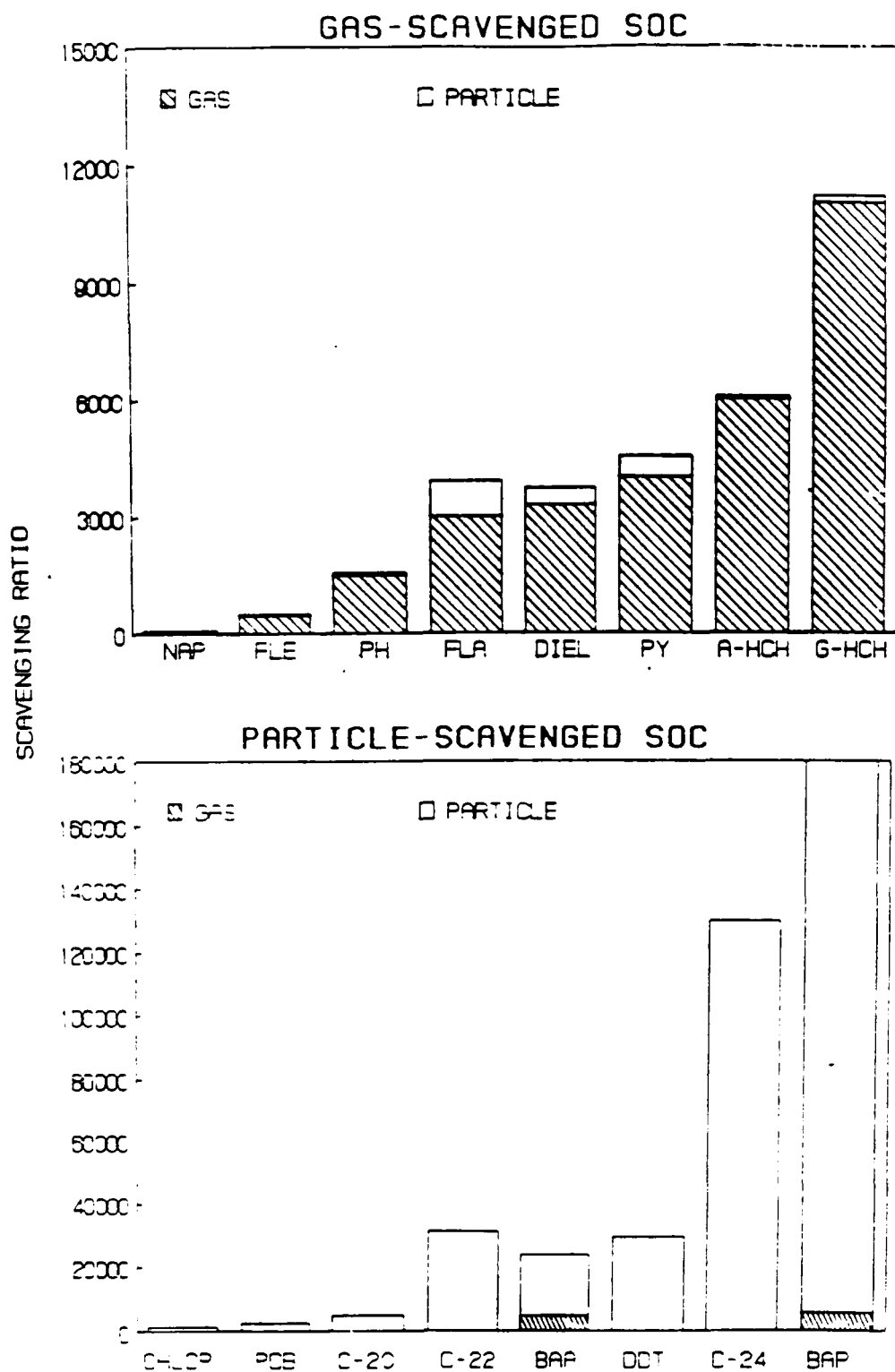
The actual situation is more complex, because of the variation in particle size distribution, re-equilibration of SOC between the gas and particle phases during rain events, emission of SOC into the atmosphere during rain events, and differences in meteorological conditions. Recent kinetic models have been formulated to take these factors into account (Tsai *et al.*, 1991; Seinfeld *et al.*, 1991); however these require a much more extensive list of input variables, including the particle size distribution of the SOC (which is often not available).

In rural air at moderate temperatures the simple Equation 2 model predicts that gas scavenging dominates for 2-3 ring PAHs, hexachlorocyclohexanes (HCHs), and dieldrin. Particle scavenging is more important for higher-ring PAHs, PCBs, n-alkanes, chlordane, and DDT (Bidleman, 1988, 1991; Swackhamer and Eisenreich, 1991; Figure 3). Rainfall removal of PCDDs and PCDFs changes from a gas to a particle-dominated process as molecular weight increases (Eitzer and Hites, 1989b; Koester and Hites, 1992).

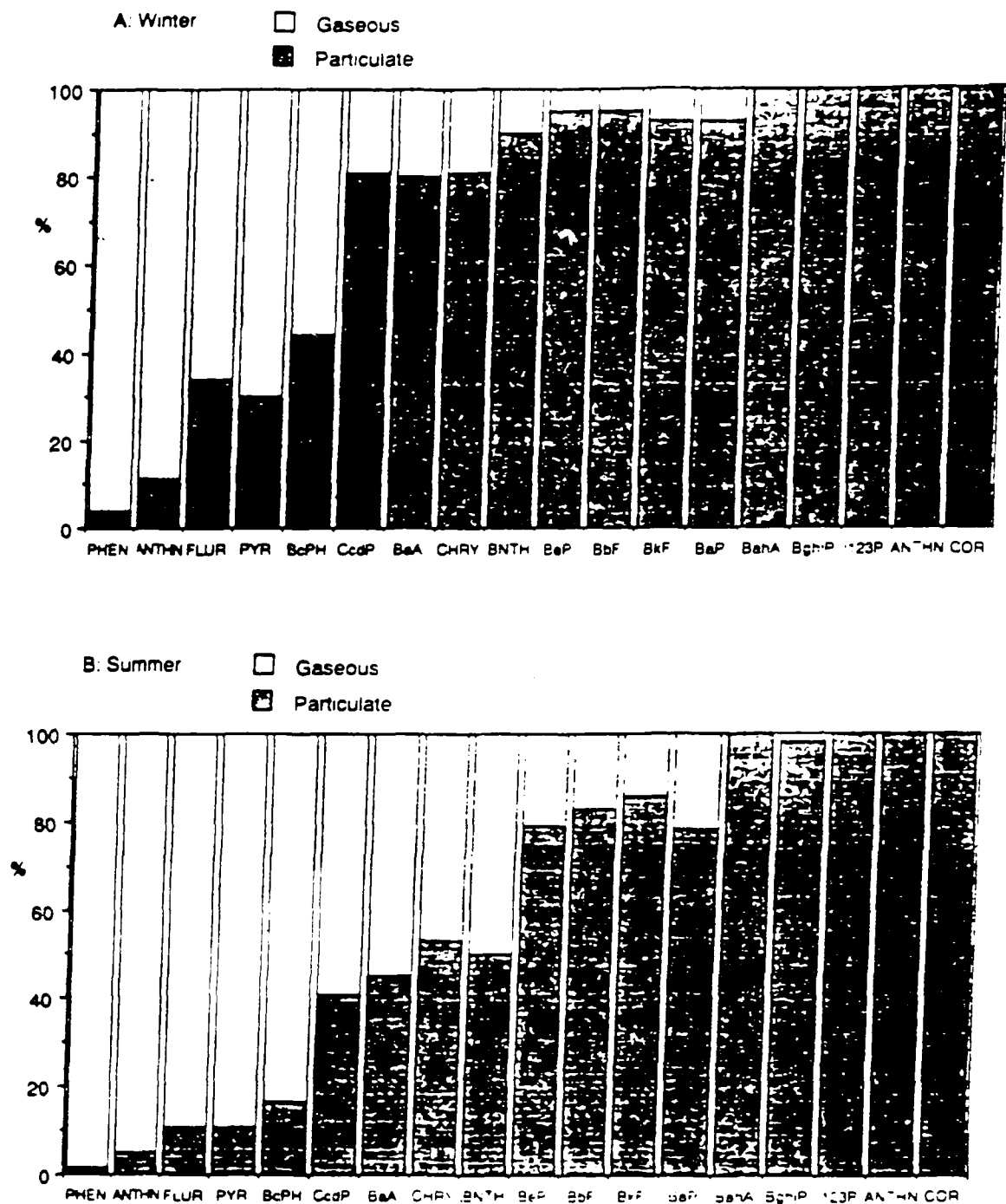
Deposition of SOC is a highly temperature-dependent process. Lowering of compound vapor pressure in winter increases the particulate fraction according to Equation 1. This can be clearly seen in Figure 4, where proportions of PAHs in the gas and particle phases during winter and summer are compared. Henry's law constants also decrease at lower temperatures, resulting in greater gas solubility in rain and cloud droplets. The overall effect is more efficient deposition of SOC in winter than in summer.

Differential removal by physical processes is one reason why profiles of SOC at receptor sites differ from those at sources. The case of PCDDs and PCDFs is a good example. Profiles of PCDDs and PCDFs from municipal incinerators and industrial waste effluents (Czuczwa and





**Figure 3.** Calculated overall wet scavenging ratios ( $W_p$ , Equation 2) for SOCs that are removed predominantly by gas (upper) and particle (lower) deposition. For each compound the proportion scavenged by each process is shown. Source: Bidleman (1991).



**Figure 4.** Relative proportions of PAHs in the gaseous and particulate phases during winter and summer, as determined by high volume air sampling. Source: Baek *et al.* (1992).

Hites, 1986) and ambient air (Broman *et al.*, 1991a; Eitzer and Hites, 1989a,b; Smith *et al.*, 1990) show the presence of compounds containing 4-8 chlorines. Because particulate fractions are greater for the more highly chlorinated homologs, rain and dry flux distributions are weighted toward compounds containing 7-8 chlorines (Eitzer and Hites, 1989b; Koester and Hites, 1992). Atmospheric degradation of gas-phase PCDDs and PCDFs may also contribute to profile alteration (Koester and Hites, 1992). The result is that PCDDs and PCDFs in Great Lakes sediments are dominated by 7- and 8-chlorinated compounds (Czuczwa and Hites, 1986; Eitzer and Hites, 1989b; Koester and Hites, 1992; Figure 5).

### 3.4.1 Alteration of PAHs in the Environment

The problem of selective physical removal of SOC's from the atmosphere and the effect on chemical profiles has been discussed earlier. In addition, PAHs can undergo chemical and photochemical reactions in the atmosphere that lead to changes in the relative proportion of compounds between source and receptor.

Many studies have been done to determine reactivities of PAHs in the gas and particle phases, with sometimes contradictory results. Light, mixtures of oxidant gases, and the particle composition all influence the rate of PAH degradation (Daisey *et al.*, 1986; Greenburg *et al.*, 1985). The latter authors found good correspondence between experimental PAH stabilities and those predicted from molecular properties.

Laboratory studies show that PAHs are more stable to photolysis when adsorbed to fly ash than on artificial substrates like alumina, silica gel, or glass (Yokley *et al.*, 1986). Among the fly ashes, those with high carbon content and black or gray were most effective in stabilizing adsorbed PAHs (Behymer and Hites, 1988; Dunstan *et al.*, 1989; Yokley *et al.*, 1986).

Kamens *et al.* (1988-90) found rapid degradation of PAHs on wood smoke particles when exposed to natural sunlight. At moderate temperatures and humidities, PAHs decayed within an hour. At low temperature and humidity and reduced light intensity the time scale for PAH loss increased to days. Oxygenated PAHs were stable to sunlight alone, but labile in the presence of 0.2 parts-per-million (ppm) ozone and sunlight. Sunlight was the most important factor causing loss of benzo(a)pyrene (BaP) from wood soot, followed by ozone and nitrogen dioxide. Guo and Kamens (1991) estimated a BaP half-life of 80 h on wood smoke particles for reaction with 0.2 parts-per-million atmospheric NO<sub>2</sub>. PAHs on diesel particulate matter were converted by exposure to part-per-million levels of ozone over a few hours (Van Vaeck and Van Cauwenberghe, 1984).

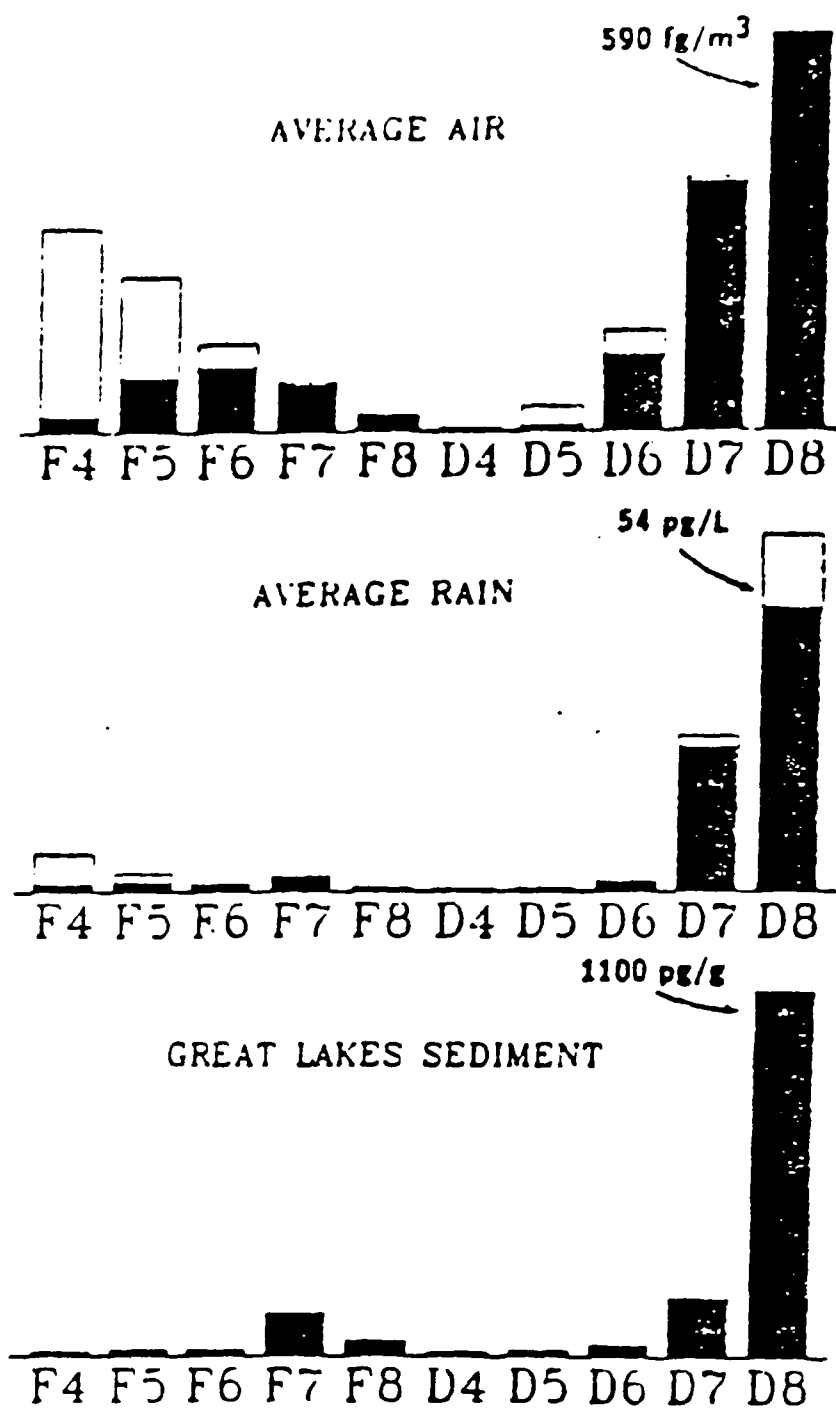


Figure 5. Homolog profiles of PCDFs (F4 - F8) and PCDDs (D4 - D8) containing 4-8 chlorines in air and rain from Bloomington, Indiana, and in Great Lakes sediments. Source: Eitzer and Hites (1989b).

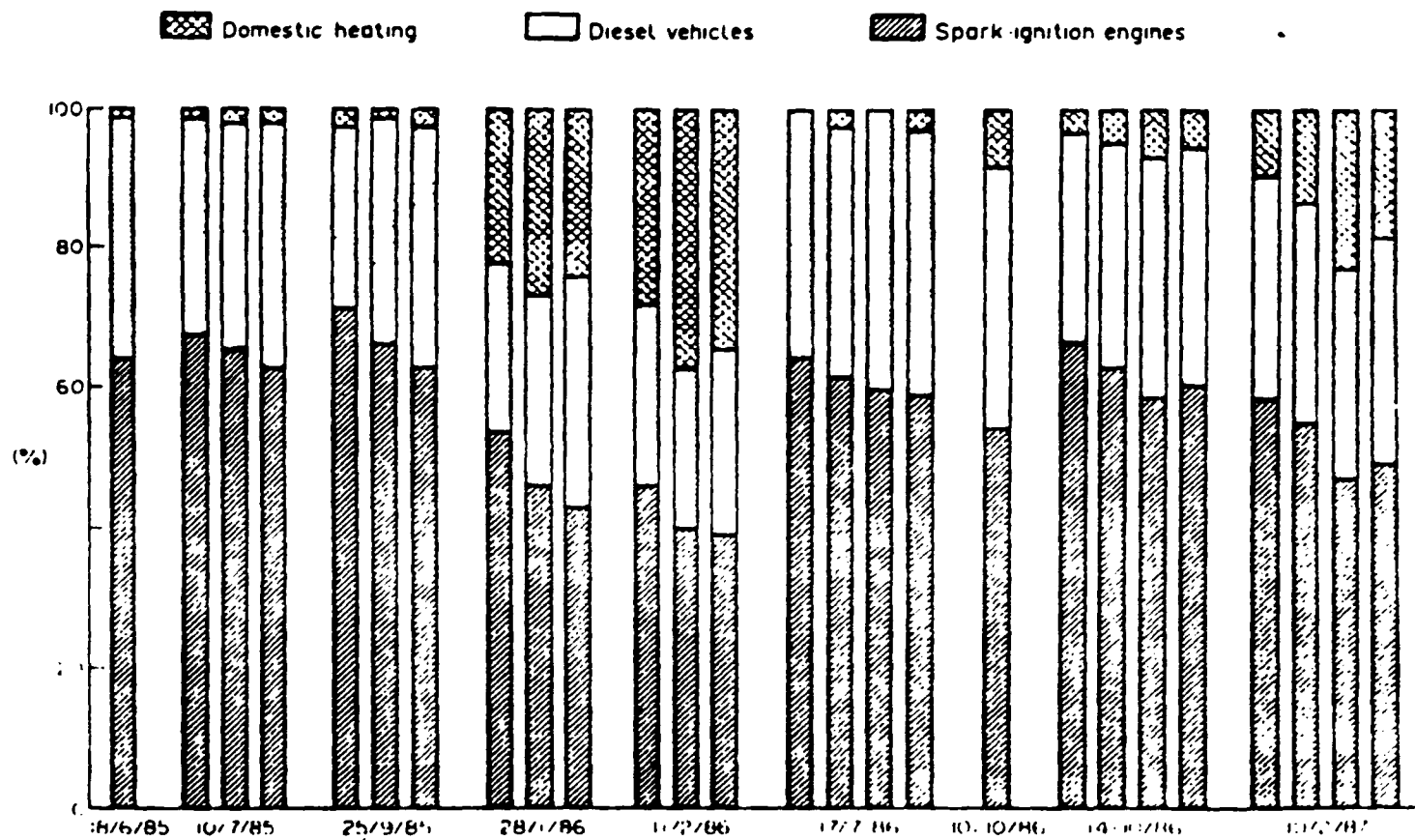
Losses of parent compounds does not necessarily represent a gain for the environment. Indeed, reaction of PAHs with atmospheric oxidants leads to formation of PAH oxones and PAHs substituted with hydroxy- and nitro-groups, some of which are highly mutagenic (Arey *et al.*, 1987; Kamens *et al.*, 1985; Kleindienst *et al.*, 1986; Nishioka *et al.*, 1988; Nishioka and Lewtas, 1992; Ramdahl *et al.*, 1986).

A different picture of PAH reactivity is seen from field studies. Freeman and Cattell (1990) found that although diurnal variations in total PAH occurred in urban air, ratios among the PAHs were fairly constant. Gibson *et al.* (1986) examined ratios of BaP to lead and elemental carbon (EC) in coastal Delaware and Bermuda. The expected reduction in BaP following long-range transport did not occur; BaP/Pb and BaP/EC were approximately the same in the two locations. However the BaP/EC ratio in Detroit was much higher than in Delaware or Bermuda. To explain the difference between the inner city and Delaware/Bermuda ratios, the authors suggested that BaP is rapidly reduced to a low level as particulate matter ages, after which further losses are slow. Evidence of atmospheric transformations of other PAHs during transport were found from elevated proportions of nitro- and hydroxynitropyrenes to inert markers in Bermuda compared to Delaware. The ratio of reactive/unreactive PAHs on aerosols was about the same in stationary southern Norway air compared to air transported from the United Kingdom and France (Bjorseth *et al.*, 1979).

A method for correcting PAH profiles for degradation and/or physical removal effects during transit was suggested by Masclet (1986). A "relative decay index" (RDI) was established based on the diurnal variation of each PAH concentration in urban air. This RDI concept was used in a CMB model for PAHs in Paris air (Pistikopoulos *et al.*, 1990). PAH profiles in ambient air were matched against profiles of six 5-6 ring PAHs from three sources: spark-ignition and diesel engines, and domestic heating. Losses of PAHs due to differential reactivity were accounted for by summer and winter RDIs. Spark-ignition vehicles accounted for 40-70% of these PAHs, and diesels for 20-40%. The contribution from domestic heating rose from a few percent in summer to 20-40% in winter (Figure 6).

### **3.4.2 Alteration of PCDDFs in the Environment**

Degradation of PCDDFs during transport has not been given the attention received by PAHs. Gaseous species are photosensitive (Podoll *et al.*, 1986) and reactive toward hydroxyl radicals (Table 1). PCDDFs in natural waters (Friesen *et al.*, 1990) and on fly ash (Tysklind and Rappe, 1991) can be photolyzed in solution. Penta- and hexa-CDDs were photo-reactive when exposed to natural sunlight in distilled water - acetonitrile solution, and the photolysis rate was



**Figure 6.** Contributions to total PAHs in Paris air, calculated by CMB. Source: Pistikopoulos *et al.* (1990).

markedly increased in natural water -acetonitrile. Projected half-lives in sunlit surface waters were 27-81 days. The sensitized photolysis may have been due to humic materials (Friesen *et al.*, 1990). Less chlorinated PCDDs are also photolyzed in water (Dunlin *et al.*, 1986). Koester and Hites (1992) noted that profiles of PCCDFs in urban and rural areas were different, and suggested that a combination of phase distribution effects and gas-phase reactivity might be responsible.

### **3.5 Applications of source apportionment techniques for organics**

#### **3.5.1 Volatile organic compounds (VOCs)**

Comparative ambient air concentrations and profiles of individual VOCs in major U.S. cities, taken from a national database for VOCs (Shah and Heyerdahl, 1988), were presented by Edgerton *et al.* (1989a). Similarities between aromatic hydrocarbon profiles in several cities and their correspondence to an average auto exhaust profile suggested that auto exhaust was probably the dominant source. Profiles of industrially related chlorinated and fluorinated hydrocarbons showed distinct differences among the cities, depending on the source types.

Source profiles and CMB models have been used to apportion VOCs in several U.S. cities and urban areas from around the world (Aronian *et al.*, 1989; Doskey *et al.*, 1992; Kenski *et al.*, 1991; Scheff *et al.*, 1989; Scheff and Wadden, 1991; Sweet and Vermette, 1992). These papers describe in great detail the characteristic "fingerprints" of different VOCs in sources such as vehicle exhaust, gasoline vapors, industrial emissions (refineries, coke ovens, chemical plants), architectural coatings (paints, thinners, and cleanup solvents), dry-cleaning, degreasing, and graphic arts (printing). Examples of CMB apportionment of total hydrocarbons are given in Table 2 for three cities

A check on the accuracy of CMB results is to compare them with independent emissions inventories. This was done by Kenski *et al.* (1991) and Scheff *et al.* (1989) for Chicago, Detroit, and Beaumont, Texas (see Table 2). In Detroit, CMB calculations and emissions inventories agreed well for vehicles, gasoline vapor, coke ovens, and architectural coating contributions. The emission from coke ovens was confirmed by close correlation between CMB modeling coefficients and a source-based score derived from Gaussian plume dispersion models. Detroit CMB results were high for refineries and graphic arts sources. In Chicago, agreement between CMB and inventory results was good for all source categories except refineries, for which the CMB model again gave high values. The opposite was the case in Beaumont, where inventoried emissions from refineries and gasoline vapor exceeded those modeled by CMB. Very good agreement between CMB and inventory was found for a polyethylene manufacturing plant.

TABLE 2. Percent Contributions of Various Sources to Total Hydrocarbons in Three Cities:  
Comparison of Emission Inventories with Chemical Mass Balance Results<sup>a</sup>

<u>Source</u>	<u>Detroit</u>		<u>Chicago</u>		<u>Beaumont</u>	
	<u>INV</u>	<u>CMB</u>	<u>INV</u>	<u>CMB</u>	<u>INV</u>	<u>CMB</u>
<b>Vehicles</b>	32.9	28.2	35.1	41.2	11.9	13.6
<b>Gasoline Vapor</b>	6.9	9.4	7.6	6.4	4.2	19.5
<b>Point Sources</b>						
Refineries	0.7	16.5	1.3	13.5	23.1	9.1
Polyethylene Mfg.					7.3	7.0
Other Chem. Plants					35.6	
Rubber Mfg.					13.4	
Wood Pulp & Paper					1.3	
Coke Ovens	2.0	3.7				
<b>Coatings</b>						
Architectural	3.8	2.5	5.5	6.2		0.6
Industrial	14.0					
<b>Graphic Arts</b>	0.7	4.7	9.8	11.0		1.4
<b>Other</b>	38.8	34.5	40.6	16.5		

a) Source: Kenski et al., 1991, Tables 6 and 7.

CMB models, factor analysis, and wind trajectories were used to investigate VOC sources in southeast Chicago and East St. Louis by Sweet and Vermette (1992). The three techniques, if applied appropriately, are complimentary in nature. Factor analysis requires no a priori knowledge of sources and is useful for confirming the importance of known emissions or suggesting sources not inventoried (Sweet and Vermette, 1992). In southeast Chicago, factor



analysis indicated that four sources types accounted for 78.4% of the variance in the observed data: The first and largest factor was attributed to urban air sources (perhaps a combination of vehicle emissions, gasoline evaporation, and solvent emissions). A second factor identified only with benzene was assigned to coke oven combustion. The third factor comprising carbon tetrachloride and chloroform was attributed to a regional source outside the city. A fourth and unknown factor was characterized by chlorobenzene.

CMB results showed that under average conditions most aromatics resulted from vehicle exhaust. Trichloroethane, trichloroethylene, and tetrachloroethylene came from degreasing solvents and dry-cleaning. In east St. Louis, a factor associated with several aromatics and light chlorinated compounds was identified with a local chemical plant on the basis of wind trajectory analysis.

Sweet and Vermette also showed how the situation in south-eastern Chicago can deviate from the average during a pollution episode. During one event, 72% of the benzene and 17% of the ethylbenzene were released by coke ovens (Table 3). A high proportion of benzene in coke emissions was also found by Kenski *et al.* (1991). By apportioning total VOCs with assumed factors, Blakley and Klevs (1990) assigned highest releases of benzene to counties at the south end of the lake which had large coke emissions.

Pollution sources in the Kanawha River Valley, West Virginia were examined using factor analysis of VOC and trace element data (Cohen *et al.*, 1991a,b). The valley contains numerous sources of VOCs, including eleven large industrial complexes that use, store, produce, and transport organic chemicals. Only at one site were aromatic VOCs identified with an "automobile" factor, which was defined by lead, bromine, and particulate carbon. At other locations in the valley, VOCs could not be apportioned to any one factor, but instead were ascribed to a factor called "general VOCs". The "general VOC" factor differed little among sites and was not associated with total particles or element-speciated particulate matter.

The authors (1991b) discussed the difference between their source apportionment of VOCs in Kanawha River Valley and the receptor modeling results of Stevens *et al.* (1989) in Boise, Idaho. In the latter study several aromatic hydrocarbons showed excellent correlations to fine particulate lead (a gasoline source that is rapidly decreasing). These tracers were useful as a lead replacement for estimating the contribution of vehicles to ambient concentrations of fine particulate extractable organic matter (Zweidinger *et al.*, 1990).

TABLE 3. Contribution of Sources to Individual VOC Concentrations for a South Chicago Sample During a Pollution Episode<sup>a</sup>.

	<u>Coke</u> <u>Ovens</u>	<u>Vehicle</u> <u>Exhaust</u>	<u>Paint</u>	<u>Gasoline</u> <u>Vapor</u>	<u>Degreasing</u> <u>Solvent</u>	<u>Dry</u> <u>Clean.</u>
Benzene	71.6	26.3	0.6	2.3	0	0
Toluene	0.8	45.6	52.0	1.8	0	0
Ethyl-benzene	17.0	68.3	9.4	5.3	0	0
m,p-xylene	8.3	71.8	18.4	1.8	0	0
o-Xylene	1.4	66.6	30.3	1.4	0	0
1,1,1-Tri-chloroethane	0	0	0	0	100	0
Trichloro-ethylene	0	0	0	0	100	0
Tetrachloro-ethylene	0	0	0	0	12.9	87.1

a) Source: Sweet and Vermette, 1992; CMB results.

According to Cohen, the failure of VOCs to show a clear relationship to lead in Kanawha Valley might have been because: a) there were similar VOC sources at all sites, b) there was good mixing of pollutants in the valley, and/or c) the sources of VOCs were regional. These studies point out the value of using elemental and particulate information in addition to VOCs to speciate source types.

Some of the longer-lived halocarbons (e.g. methylchloroform, tri- and tetrachloroethene) have been used as "tracers of opportunity" to document pollutant transport out of the Los Angeles basin to the Nevada - Arizona desert (Bastable *et al.*, 1990; Pryor and Hoffer, 1992; Miller *et al.*, 1990; White *et al.*, 1990). Methyl-chloroform has a distinctly weekly cycle, being high during the week and dropping to near-baseline values on weekends. This cycle has been

attributed to releases of methylchloroform from metal fabrication and electronics industries in the basin (White *et al.*, 1990). Haze episodes leading to reduced visibility were correlated with elevated concentrations of methylchloroform (Miller *et al.*, 1990).

The concentrations of trace gases, such as chlorofluorocarbons, chlorocarbons and carbon monoxide were also applied in the statistical methods to discuss the sources and their contributions to the contamination at remote receptors (e.g. Khalil and Rasmussen, 1984). It was concluded that the ratios between these gases can be used as global tracers due to their distinct and different application pattern.

The concentration ratios of light hydrocarbons, such as ethane and propane to chlorinated ethenes have been used as signatures of emissions from natural gas exploitation regions as compared with emissions from regions with extended application of industrial solvents (e.g. Hov *et al.*, 1984). It was indicated that the use of chlorinated ethenes is primarily confined to industrialized countries.

### **3.5.2 Semivolatile organic compounds (SOCs)**

#### **A. Polycyclic Aromatic Hydrocarbons (PAHs)**

Unlike VOCs, very little work has been done to relate PAHs in ambient air to their sources through CMB or factor analysis modeling. This is because emission factors have been in short supply, and even within source types the quantities and ratios of PAHs emitted have been highly variable. One can see this from the examples of emission factors given in Johnson *et al.*, (1992), and also from a review of PAH profiles by Daisey *et al.* (1986). These authors critically examined literature data from the 1960s through early 1980s for PAHs in several source types. All PAH concentrations were expressed relative to benzo(e)pyrene (BeP) because this compound is fairly stable and is found almost exclusively in the particulate phase. PAH profiles were examined from auto exhaust (gasoline and diesel), residential coal and wood combustion, oil- and coal-fired power plants, and industrial coal-fired boilers.

Interpretation of PAH data is plagued by uncertainties due to sampling and analytical artifacts. PAHs occur in particulate and gaseous forms, and atmospheric concentrations will be inaccurate unless both species are collected. This has generally been done for source sampling, but until the early 1980s most ambient air PAHs were collected with filters only and concentrations of 2-4 ring compounds were seriously underestimated. Both the particle- and gas-phase compounds are mutagenic (Tuominen *et al.*, 1988; Westerholm *et al.*, 1991; Lewis *et al.*, 1988), providing another reason for collecting the two fractions. PAHs can undergo reactions

with oxidant gases during sampling, thus changing their proportions. Sample extraction and analytical methods vary among laboratories and quality assurance information is not always provided. According to the Daisey review, the three most critical factors limiting intercomparability of the organic source emission profiles reviewed by them were: a) The incompatibility of source emissions and ambient aerosol sampling methods and intervals, b) The general lack of emission profiles which represent an average for a given source type, and c) Differences in organic profiles due to variations among sampling and analytical methods rather than in source emissions.

The conclusions of Daisey were that existing data provided some useful information with respect to receptor modeling. PAH profiles from two source types that had been repeatedly sampled and analyzed by the same investigator appeared to be fairly reproducible: coke ovens and coal-fired boilers. Profiles from wood combustion varied widely and depended on combustion conditions. Cyclopenta(cd)pyrene was especially enriched in exhaust from spark-ignition engines and was suggested as a useful marker compound. Coronene and benzo(ghi)perylene were also relatively high in vehicle exhaust compared to other sources. Other organics having potential as marker compounds were retene and levoglucosan for wood combustion, and benzo(b)naphtho(2,1-d)-thiophene (BNT) for diesel engines and fuels containing sulfur.

Since the time of the literature covered in the Daisey review, sampling and analytical methods for PAHs have improved greatly. Filters followed by adsorbent traps to catch gas-phase PAHs are now in routine use for ambient air sampling. The availability of standard reference materials for urban air particulate matter and diesel particles has improved quality assurance (Wise *et al.*, 1986; 1988). PAH emission factors and profiles in a large number of source types have been compiled (Johnson *et al.*, 1992). Nevertheless, it is interesting to note that many of the reservations expressed in the Daisey review about data quality and availability were echoed in this 1992 report.

The three PAHs cited as vehicle exhaust markers by Daisey *et al.* (1986) and Baek *et al.* (1991a,b) are hardly unique. High levels of coronene were also produced by burning certain types of vegetation (Freeman and Cattell, 1990). The Johnson survey found a high ratio of benzo(ghi)perylene to BeP in wood stove emissions. Proportions of cyclopenta(cd)pyrene to BaP in vehicle exhaust and industrial coal combustion effluents were similar, and the former compound was elevated in wood smoke (Table 4). The Bghip/BeP ratio was much lower in wood soot than in gasoline soot for profiles presented by Kang and Kamens (1992), in contrast to the information given in the Johnson *et al.* report. Thus, ratios among the parent PAH compounds are not foolproof source indicators.

Daisey *et al.* (1986) felt that PAH data were best used in combination with other tracers for source apportionment (e.g. trace elements). Some information on PAHs and other organic compounds that may serve as "marker compounds" of a particular source type or process is discussed below and summarized in Table 4.

The proportion of alkyl homologs to unsubstituted compounds is an indicator of combustion source temperature. Low temperature combustion yields soots that are more abundant in alkylated PAHs, whereas unsubstituted (parent) PAHs predominate at high temperatures (LaFlamme and Hites, 1978). Initially it was thought that the alkyl homolog distribution in sediment cores could be used to distinguish "natural" (low-temperature) from "anthropogenic" (high temperature) combustion sources. However LaFlamme and Hites pointed out that coal combustion occurs at moderate temperatures and yields alkylated PAHs. Furthermore, they felt that differential water solubility of alkylated and parent PAHs could alter the distribution in sediments from what was initially deposited. Tan *et al.* (1992) recently reported that while wood burning produces mainly parent PAHs, low-intensity fires in forest floor waste ("duff") yields relatively high levels of alkylated phenanthrenes, cyclopenta(def)phenanthrene, and dodecahydrochrysene.

The ratio of methylphenanthrenes to phenanthrene (MP/P) is low in combustion effluents, but high in unburned petroleum products. Takada *et al.* (1990) found that MP/P in auto exhausts and asphalt were high relative to combustion products from a steam generator. Using this information, along with sulfur heterocyclic compounds, the authors concluded that PAHs in Tokyo street dust were strongly affected by automobile exhausts. Dusts from residential areas had a somewhat greater contribution from stationary source combustion products. The authors pointed out that the MP/P ratio in auto exhaust is highly variable, depending on engine load and cylinder exhaust temperature, and suggested that extensive collection of auto exhausts should be conducted. Runoff samples from urban and coastal South Carolina were depleted in MP relative to crankcase oils and diesel fuel, and showed PAH profiles similar to the atmospheric particles. The conclusion was that PAHs in street dust came mainly from atmospheric deposition and not from dripping crankcase oils (Ngabe, 1992).

Alkylphenanthrenes were also high in samples from the Baltimore Harbor Tunnel (Benner *et al.*, 1989). A comparison of tunnel air samples to standard reference diesel and urban air particulate matter showed that tunnel and diesel particles were enriched in MP. Factor analysis suggested that contributions from diesel and gasoline-powered vehicles might be separated by alkylated PAH content.

**TABLE 4. Marker Information for Identifying Sources of PAHs and Other Organic Compounds.**

<u>Source</u>	<u>Marker Compounds</u>	<u>Examples</u>
Spark-source engines	cyclopenta(cd)pyrene	Daisey <i>et al.</i> , 1986.
Diesel engines	benzo(b)naphtho(2,1-d)-thiophene	Daisey <i>et al.</i> , 1986; Alsberg <i>et al.</i> , 1989.
Motor vehicles	benzo(ghi)perylene, coronene	Daisey <i>et al.</i> , 1986 Alsberg <i>et al.</i> , 1989.
High vs. low temperature combustion & combustion vs. unburned petroleum products	parent/alkylated PAH ratios	LaFlamme & Hites, 1978; Takada <i>et al.</i> , 1991;  Ngabe, 1992.
Wood combustion	methoxyphenols & other lignin pyrolysis prod.	Hawthorne <i>et al.</i> , 1988, 1989; Edye & Richards, 1991.
Wood combustion	retene, levoglucosan carbon-14, potassium	Daisey <i>et al.</i> , 1986
Vegetation fires	alkylated phenanthrenes cyclopenta(def)phenanthrene dodecahydrochrysene	Tan <i>et al.</i> , 1992.
Vegetation fires	carbon preference index	Standley & Simoneit, 1987, 1990.
and other biogenic sources, biogenic	(CPI: odd for n-alkanes & alkanones, even for acids	Simoneit, 1989;
vs. anthropogenic hydrocarbons unresolved complex mixture	& alcohols), presence of UCM for (petroleum products), biogenic markers: retene, di- & tri-terpen phytosterol	Mazurek & Simoneit, 1984; Kawamura & Leuenberger <i>et al.</i> 1988; Gagosian & Pelzer, 1986;  Farmer & Wade, 1988; Foreman & Bidleman, 1990 Greaves <i>et al.</i> , 1987.
Tire wear	Benzthiazoles	Spies <i>et al.</i> , 1987.

As indicated by Daisey *et al.* (1986) other marker compounds may be used to advantage in differentiating PAH source contributions. BNT was used as a diesel exhaust indicator by Alsberg *et al.* (1989), who employed principal component analysis to examine profiles of PAHs and aromatic VOCs collected in Gothenburg, Sweden. Diesel and gasoline emissions were separated by enrichment of BNT and particle-associated light PAHs in the former, and aromatic VOCs and heavy PAHs (particularly benzo(ghi)perylene and coronene) in the latter. Cautions about using these two PAHs have been mentioned earlier.

Methoxylated phenols have been suggested as tracers for wood smoke pollution, which is a major contributor of PAHs (Hawthorne *et al.*, 1988, 1989). More than 70 species, arising from pyrolysis of lignin, have been identified in soot from residential wood stoves. Guaiacols in hardwood and softwood soots were nearly the same, whereas syringols were much higher in the hardwood soots. It was suggested that guaiacols could be used as markers for wood combustion in general and syringols could serve to differentiate wood type.

Simoneit (1989) reviewed the wide variety of biomarker compounds available for use in source reconciliation. These include n-alkanes and similar compounds (acids, alcohols, ketones), phytosterols, terpenoids, and terpenols. Some of these may be useful for investigating regional sources in long-range transport. For example, the signatures of C<sub>27-29</sub> phytosterols were different in aerosols from the western U.S., Nigeria, and southeastern Australia. Further work is needed to evaluate the stability of marker compounds in the atmosphere and during sampling.

Air samples from slash-burns along the Oregon coast were analyzed for a wide variety of plant wax components and terpenoids (Standley and Simoneit, 1987). PAHs accounted for only a minor part of the hexane-soluble material, most of which was plant waxes, resins, and thermally matured compounds. Smoke from the burns contained straight-chain homologs with a strong plant wax signature: n-alkanes and n-alkanones showed an odd-carbon preference, peaking at C<sub>27</sub>. Straight-chain alkanolic acids and alcohols showed an even-carbon preference. The acids peaked at C<sub>22</sub>, C<sub>24</sub>, or C<sub>30</sub>, whereas the maximum for the alcohols occurred at C<sub>22</sub>. A number of di- and triterpenoids, as well as retene, were suggested as molecular markers for this type of burn. In a subsequent study (Standley and Simoneit, 1990), polar cyclic di- and triterpenoids were analyzed in extracts of residential wood combustion aerosols. Distinct signatures were found that could be used to trace the input from coniferous, alder, and oak combustion products.

Profiles of organic compounds in atmospheric particulate matter collected in Colorado was examined by Greaves *et al.* (1987) using factor analysis. One factor associated with ozone and oxygenated compounds such as acids, furans, aldehydes, ketones, and lactones was

interpreted as arising mainly from photochemical processes. Factors 2 and 3 which contained terpenoids and odd-chain hydrocarbons were ascribed to biogenic sources. This hypothesis was strengthened by noting that factor 2 was strongly dependent on wind direction, being largest when the wind was from a national forest to the west. Factor 4, associated with CO and several long-chain alkanes, was identified with motor vehicles.

A proposed method for source characterization was based on the high-resolution gas chromatographic profile of neutral-fraction components of fine organic aerosol (particle diameter  $< 2 \mu\text{m}$ ) (Hildemann *et al.*, 1991a). A large number of source types were examined: wood combustion; automobile and truck exhausts; fuel oils; natural gas appliances; vegetation detritus; tire, brake, and road dusts; cigarette smoke; roofing tar; and charbroiled meats. The similarities or differences among these aerosol signatures were determined by hierarchical cluster analysis.

Tire wear can contribute PAHs to road dust, since carbon black is used in the rubber (Voldner and Smith, 1989). Spies *et al.* (1987) suggested using benzthiazoles, found in estuarine sediments of San Francisco Bay, as indicators of street runoff. The benzthiazoles are breakdown products of antioxidants added to tire rubber.

## B. PCDDFs

A considerable amount of work has been done to determine differences in congener profiles from various sources and relate them to environmental matrices. The use of principal component analysis (PCA) and other multivariate techniques seems to be more frequent than in PAH investigations.

Czuczwa and Hites (1986) applied PCA to differentiate sources of PCDDFs in Great Lakes sediments. Profiles of PCDDF homologs (4-8 chlorines) were compared for sediments, particulate ambient air samples, incinerator combustion products, and different PCP products. Sediments from all lakes except Ontario formed a tight cluster with ambient air particles that was separate and distinct from the incinerator or PCP patterns. Clustering of a Lake Ontario sediment core with the PCP data pointed to contamination from suspected sources on the Niagara River.

Changes in the relative proportions of PCDDFs in moving from source to receptor were investigated by Eitzer and Hites (1989b) using PCA. Homolog profiles from different urban combustion sources were widely scattered and showed no grouping tendency. Urban and industrial air samples clustered in the middle of the sources, indicating that a mixture of sources produces a fairly consistent homolog profile in ambient air. Differences could be noted between urban and suburban air groups.



Of special interest was the comparison of particulate vs. gaseous homolog profiles in air, and particulate vs. dissolved profiles in rain. Examination of homolog distributions for these individual phases by PCA clearly showed that particle-bound PCDDFs are preferentially transported to sediments, giving rise to the pattern alterations shown in Figure 5. Relative to whole (particulate + gaseous) air samples, the homolog profile of the particulate fraction moved toward the cluster for sediments, whereas the gaseous fraction moved away. The same trend was noted for particulate and dissolved components of rain samples.

PCA revealed differences between urban (Indianapolis, IN) and rural (Trout Lake, WI) air samples, indicating that changes occur during atmospheric transport. The cluster of wet and dry deposition samples was shifted away from those of whole air samples and toward the sediments (Koester and Hites, 1992).

Smith *et al.* (1990) were able to distinguish three patterns of ambient air PCDDFs in upstate New York cities by PCA, which they designated as "source-related", "common background", and "enhanced lower-chlorinated compounds". The latter samples were especially high in TCDFs. Some air samples from Niagara Falls, NY showed a "source" profile, typical of municipal waste incinerators; others showed the "common background" pattern. A background pattern was also yielded by air sample from a parking garage. The "lower chlorinated" distribution was found on consecutive hot summer days when air masses were transported from New York City and New Jersey to Albany, where the samples were taken. The authors speculated that enhancement of less chlorinated species might result from selective deposition of heavier, more particle-bound compounds, but also mentioned the possibility of other, unidentified source types.

Clues to the origin of these lower-chlorinated PCDDFs were provided by Bacher *et al.* (1992), who examined fingerprints of PCDDFs and their brominated analogs in chimney deposits from wood burning and in auto exhaust. Compounds containing 1-4 chlorines were abundant, especially for the PCDFs. Auto exhaust yielded the highest levels of brominated dibenzodioxins and dibenzofurans, most containing 1-2 bromines. The authors felt that the full homolog spectrum (1-8 chlorines) should be considered when deducing sources from environmental patterns. Rappe *et al.* (1989) also commented on the similarity of the isomeric pattern for tetra-CDDFs in air particulate samples, car exhaust, and municipal incinerator products.

Emissions data from incinerators in different countries were compared using PCA (Edgerton *et al.*, 1989). Of twelve municipal incinerators, homolog profiles for seven were tightly grouped, whereas the other five were widely scattered. Those five included three incinerators that

were burning under unsteady conditions and two that had PCDDF levels near the detection limit. The seven grouped incinerators were clearly distinguished from the well-separated clusters of three sewage incinerators and three Kraft mill boilers. Ambient air samples from Columbus, OH which were taken near both a sewage sludge and a municipal incinerator were similar to both source types. Air samples from Akron, OH were grouped in the overlapping clusters formed by municipal incinerators and traffic tunnels. Based on a survey of 400 publications on PCDDF sources, Pitea *et al.* (1989) used PCA and cluster analysis to differentiate PCDDF patterns in various types of incinerators.

Class separation of PCDDFs in human milk samples from Sweden was achieved using partial least squares analysis (Lindstrom *et al.*, 1989). One set of milk samples characterized by a relative high proportion of PCDFs (especially hexachloro-DFs) came from an area near a magnesium plant which had high emissions of these compounds.

Multivariate analysis of atmospheric data from Stockholm and Baltic areas indicated a change in PCDDF proportions in moving from the city to open coastal areas (Broman *et al.*, 1991a). Three air samples showed similarities to settling particulate matter collected in sediment traps from the Baltic. A fourth air sample more closely resembled particles from filtered water.

Homolog profiles from combustion sources and in ambient air are substantially different from those in pulp mill effluents. Combustion patterns of 4-8 chlorinated compounds, exemplified in Figure 5 show a wide range of PCDDFs. Effluents from Kraft bleaching are enriched in tetra-CDDFs, especially in toxic compounds substituted in the 2,3,7,8-positions (Amendola *et al.*, 1989; Axegard and Renberg, 1989; Clement *et al.*, 1989; Fouquet *et al.*, 1990; Swanson *et al.*, 1988). Homolog fingerprints in sediments from large Swedish lakes showed that mill-related compounds were distributed throughout the lake. These patterns could be distinguished by PCA from those in three small lakes that were atmospherically influenced (Kjeller *et al.*, 1990).

Kang and Kamens (1992) used results from laboratory chamber degradation experiments to correct PAH profiles in urban air for transformation effects. Corrected profiles were used in a CMB model to differentiate three source types: residential wood combustion, gasoline spark ignition emissions, and diesel engine emissions.

### C. Pesticides

The application of source apportionment techniques to investigate the sources of pesticides has been meagre. This is largely because of the physio-chemical nature of pesticides, how they are used, and where they are utilized. The earth's surface is a vast reservoir for

pesticides and other organic substances as well as metals such as mercury. The exchange of pollutants is a two way process with soils, plants, water bodies, etc. acting as both sources and sinks of airborne chemicals. Understanding the two-way nature of air-surface exchange is necessary if we are to interpret observed annual cycles of pesticides in the atmosphere, and eventually to understand the sources. Several investigations have shown that ambient air concentrations of OC pesticides and PCBs are higher in summer and lower in winter (Hermanson and Hites, 1989; Hoff *et al.*, 1991a; Lane *et al.*, 1992a; Larsson and Okla, 1989; Manchester-Neesvig and Andren, 1989)(Figures 4, 7). Differences in summer-winter fluxes of PCBs in Green Bay (Achman *et al.*, 1992) and HCHs in the Great Lakes (McConnell *et al.*, 1992) have been observed.

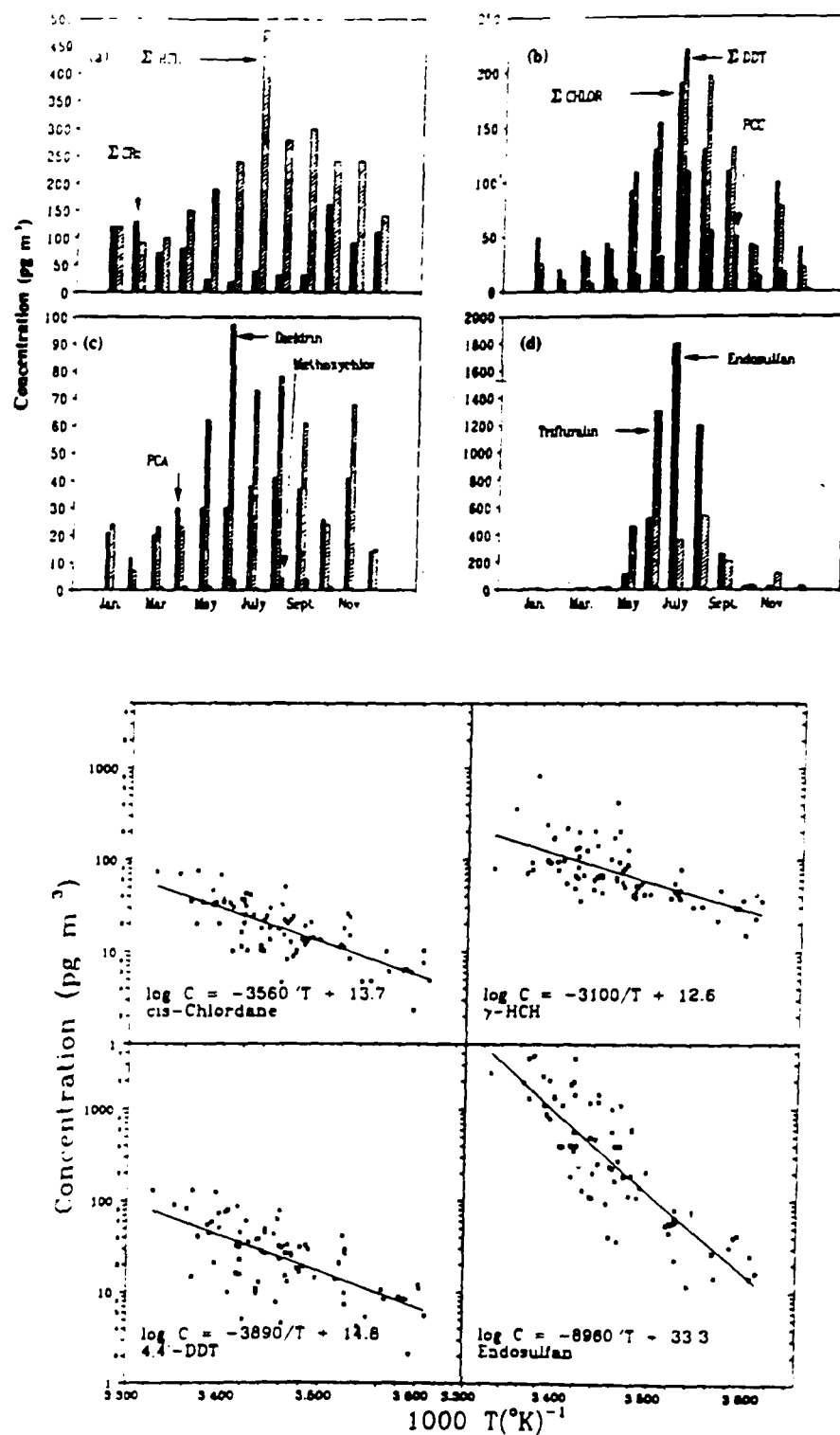
The temperature effect on these processes can be simply described by the relationship:

$$\text{Log H (or P)} = m/T + b \quad (7)$$

where H or P are the Henry's law constant or vapor pressure of the compound and T is the ambient temperature (Kelvin). The seasonal cycle of pesticides in air at Egbert, Ontario are reasonably well described by Equation 7 (Hoff *et al.*, 1991b, Figure 7). Similar trends were found for HCHs in the Great Lakes region (Lane *et al.*, 1992b) and chlordane in Columbia, South Carolina (Bidleman, unpublished data). The plant-air BCF is related to H through Equation 6.

The implication is that concentrations of pesticides and PCBs in ambient air are controlled by take-up and degassing from soil and plant surfaces. New emissions of pesticides are thus super-imposed on this background, the magnitude of which varies seasonally and regionally. A significant problem is distinguishing local surface exchange phenomena (Equations 6 and 7) from transport- and usage-related events. For example, did the high endosulfan concentrations observed at Egbert (Figure 7) result from volatilization or local summertime use of the chemical? Were elevated DDT and chlordane concentrations at Egbert due to temperature controlled local volatilization, or the fact that warm air masses were transported from the southern U.S.? Trajectories shown by Hoff *et al.* (1991b) do indeed show that high concentrations of DDT, chlordane, and other OCs were associated with southerly airflow.

The answer is that all of these phenomena are related, and at present we cannot decouple local surface exchange effects from transport. The ability to do this is important to understanding current sources of OC pesticides and PCBs to the Great Waters.



**Figure 7.** Annular cycles of pesticides at Egbert, Ontario, 1988-1989 (Hoff et al., 1991a,b). Top: Monthly trends of chlorobenzenes (CBz) and several pesticides (PCC=toxaphene). Bottom: Equation 6 plots of atmospheric concentration (log) vs. reciprocal temperature.

### Isomeric Ratios of Pesticides

Many technical pesticides, especially OCs, are mixtures of several isomers and related compounds. Relationships among these species provide clues to sample history and source, however ambiguities result from the use of products having different isomeric contents. Differential reactivity of isomers also results in changes in their relative proportions which are not well understood. Examples of compound ratios as source indicators are given below.

**Hexachlorocyclohexanes.** Technical HCH (formerly called "BHC") consists of five isomers:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ . The isomer in highest proportion is  $\alpha$ -HCH, accounting for 55-70% of the mixture. The only insecticidally active species,  $\gamma$ -HCH, is present at only about 8-15%. Technical HCH is heavily used in Asia; India alone accounts for over 20,000 metric tons/y. Mexico also uses technical HCH (FAO, 1986-89). Ratios of  $\alpha$ -HCH/ $\gamma$ -HCH in various technical HCH products range from 0.6-15; 4-5 has been found in mixtures from two heavy-use countries, India and China (Bidleman *et al.*, 1992b). Technical HCH has been banned in Canada (1971) and the U.S. (1978), and replaced by much smaller quantities of lindane (pure  $\gamma$ -HCH). Lindane is also used exclusively in western Europe.

Atmospheric samples in the Northern Hemisphere show a global background of  $\alpha$ -HCH with spikes of  $\gamma$ -HCH from regional use of lindane. Air samples from India show  $\alpha$ -HCH/ $\gamma$ -HCH in the 2-8 range, whereas the same ratio is 0.2-1 in Europe (references in Bidleman *et al.*, 1992a,b). In the Great Lakes region  $\alpha$ -HCH/ $\gamma$ -HCH ranges from near unity to 20 (Lane *et al.*, 1992b). A springtime minimum in this ratio at Egbert (Hoff *et al.*, 1991a) and Green Bay (McConnell, 1992) may reflect regional use of lindane as a seed treatment. Lane *et al.* (1992b) observed a three-fold increase in the concentration of  $\alpha$ -HCH at Point Petre accompanying airflow from the S-SW. As a user of technical HCH, Mexico may be the source.

A confounding factor in interpreting  $\alpha$ -HCH/ $\gamma$ -HCH ratios is possible interconversion or selective removal of the isomers. Several studies (referenced in Bidleman *et al.*, 1992a) have demonstrated that  $\gamma$ -HCH is slowly transformed to  $\alpha$ -HCH in soils and sediments by microbial action. Suggestions have been made that this transformation also takes place in the atmosphere and may account for the exceptionally high  $\alpha$ -HCH/ $\gamma$ -HCH ratios observed in some Arctic air samples (Pacyna and Oehme, 1988). No experimental evidence has been found to confirm or deny this hypothesis. Ballschmiter (1991) called into question the isomerization of  $\gamma$ -HCH in the atmosphere by noting that  $\alpha$ -HCH/ $\gamma$ -HCH ratios are typically much lower in the Southern Hemisphere, where use of lindane is more prevalent. If atmospheric chemistry is responsible for

the high proportion of  $\alpha$ -HCH in the Northern Hemisphere, these processes should take place in the Southern Hemisphere as well.

**DDT and Related Compounds.** Technical DDT contains about 70-80% of p,p'-DDT, the insecticidal isomer, 20-30% o,p'-DDT, and minor percentages of other isomers and impurities. In the environment, the DDTs are transformed to a greater or lesser extent into DDEs (p,p'-DDE and o,p'-DDE) and DDDs (p,p'-DDD and o,p'-DDD). Polar metabolites are also formed, but their use as markers has so far not been exploited.

DDT has a very long lifetime in soils. A 1985 survey of California soils -- 13 years after the ban of DDT -- revealed detectable residues at every one of the 99 sites tested (Mischke *et al.*, 1985). During this time substantial changes had taken place in the relative proportions of DDT compounds. The average ratio of DDTs (sum of p,p'-DDT and o,p'-DDT) to total DDT residues (DDTs + compounds in the above paragraph) in soils averaged 0.49. Thus, about half the DDT was broken down to DDE and DDD compounds.

Since DDE has a higher vapor pressure than either DDT or DDD, residues volatilizing from soils treated long ago ("old" residues) would be expected to contain predominantly DDE. The composition of vapors from technical DDT that is freshly applied or evaporated from soils treated relatively recently should be enriched in the parent compounds, p,p'-DDT and o,p'-DDT. This information allows judgments to be made concerning "old" and "new" sources of the chemical.

Peat cores from the Great Lakes region and eastern Canada showed peak DDT accumulations in the late 1960s, but surface samples representing the 1980s still contained DDT residues. Moreover, the composition of this freshly deposited DDT was largely p,p'-DDT and o,p'-DDT. These findings led Rapaport *et al.* (1985) to the hypothesis that fresh DDT was being transported to the Great Lakes region, possibly from use in Mexico and Central America.

The composition of DDT residues in peat cores may not be reflective of what is in the atmosphere because of differential deposition by precipitation and fallout. Since the DDTs have lower vapor pressures, they are present to a greater extent on atmospheric particles and more amenable to deposition. Examination of DDT/DDE ratios in atmospheric samples from different areas of the world shows the effect of age on residue composition (Table 5). High levels of total airborne DDT have been found in India, Congo, and Irkutsk (Siberia), indicating recent usage (McConnell, 1992). In all of these locations the proportion of DDT/DDE was high. The ratio was lower, but still above unity at Lake Baikal, which was probably the recipient of long-range

atmospheric transport. In North America, the proportion of DDE has increased with time. This is exemplified by the decrease in DDT/DDE in Denver from 2.0 in 1980 to 1.2 in 1986. A nine-state survey of airborne pesticides in 1970-71 showed average DDT/DDE = 2.6 (referenced in Bidleman *et al.*, 1976). Larsson and Okla (1989) noted that DDT/DDE in atmospheric fallout in Sweden had decreased significantly, from 4.1 in 1972-73 to 2.6 in 1984-85.

TABLE 5. Ratios of DDT/DDE in Ambient Air.

Location	Year	DDT/DDE	Reference
Lake Baikal, Siberia	1991	1.2	McConnel, 1992
Irkutsk, Siberia	1991	2.5	McConnel, 1992
Brazzaville, Congo	1989	3.2	Ngabe & Bidleman, 1992
India (Several towns)	1980-82	1.8	Kaushik <i>et al.</i> , 1987
Porto Novo, India	1987-89	"mostly DDT"	Ramesh <i>et al.</i> , 1989
Denver, Colorado	1980, 1986	2.0, 1.2	Foreman & Bidleman, 1990
Egbert, Ontario	1988-1989	0.4	Hoff <i>et al.</i> , 1991a
Great Lakes	1990	0.8	McConnel, 1992
Alert, N.W.T.	1988	0.6	Patton <i>et al.</i> , 1991

Current DDT/DDE ratios in air from the Great Lakes region are typically <1. Nevertheless there are some situations in which DDT/DDE > 1 are observed in North America. McConnell (1992) gives ratios of DDT/DDE for samples collected in 1989-90 in the Great Lakes region. One sample taken in Green Bay during June, 1989 showed DDT/DDE = 1.8. This sample was also enriched in toxaphene and chlordane, and was associated with airflow from the S-SW. Another air sample from Lake St. Clair in August, 1990 contained unusually high levels of DDTs and DDT/DDE = 2.4. Trajectory information has not yet been obtained for this sample. Although preliminary, these observations suggest that pulses of "new" DDT are being superimposed on a North American background of atmospheric residues that are largely DDE.

The source of this "new" DDT is unclear. Usage in Mexico and Central America is often assumed to be responsible, because of the DDT/DDE relationships for "old" soils discussed above. However a recent report documented long-term persistence of parent DDT -p,p'-DDT -- in soils from New Mexico and Texas (Hitch and Day, 1992). Some of these soils contained five times as much DDT as DDE when sampled in 1985. Investigation of the DDT/DDE ratio in combination with air trajectory information should be useful for locating such regional sources.

**Chlordane Isomers.** The ratio of trans-/cis-chlordane (TC/CC) in technical chlordane is about 1.3. Because TC is slightly more volatile, the predicted vapor-phase ratio is 1.7. Average TC/CC ratios in air samples from a source region (Columbia, South Carolina) are close the latter value (Bidleman *et al.*, 1990). As chlordane undergoes atmospheric transport, the TC is depleted and TC/CC decreases. Ratios from various locations removed from North America show this effect: Sweden 1.3, Sable Island 0.9, summer Arctic 0.5-0.6, winter Arctic 1.0, Lake Baikal (Siberia, summer) 0.6 (Bidleman *et al.*, 1990, 1992c; McConnell, 1992). The situation at Sable Island was interesting because it suggested differences between regional transport and the global background. Air samples showing 80% transport from the S-SW showed TC/CC = 1.1-1.3. By comparison, when air masses arrived mainly from the N-NW, TC/CC dropped below unity. TC/CC in air samples at Egbert, Ontario showed an annual cycle, about 0.8-1.0 in summer and 1.2-1.5 in winter (Hoff *et al.*, 1991a).

Reasons for these isomeric changes have not been determined. TC is more labile in soils, and thus old residues might be expected to contain higher proportions of CC. Changes in this ratio, as well as those of DDT/DDE might occur if these pesticides move by the "grasshopper effect", continually being deposited and revolatilized from soils. It is unknown if chlordane isomers are decomposed in the atmosphere.

Recently a new technique has been developed which may help distinguish "old" from "new" sources -- the ability to separate optical isomers by gas chromatography. Like amino acids, certain pesticides have "right" and "left" handed isomers. These enantiomers have identical chemical and physical properties and are thus not distinguishable by normal analytical methods. The development of chiral-phase capillary gas chromatography columns allows their separation. The technique allowed Muller *et al.* (1992) to determine that, whereas the two enantiomers of  $\alpha$ -HCH were in a 1:1 ratio in the technical pesticide, alterations in this ratio occurred in soil, rain, and tissue samples. Because only enzymatic processes can change the enantiomeric ratio, this is evidence for biological alteration of residues which are reflected in atmospheric samples (rain).



#### D. PCBs

Little work has been done to link PCB residues in receptors to their sources through examination of congener profiles. This is probably because of: a) Lack of routine use of high-resolution analytical methods, b) Poor interlaboratory comparability because of different numbers of congeners included in the analysis, c) Poor information on PCB profiles from different sources, and d) Changes in PCB profiles in the environment.

In the 1960s and most of the 1970s, analysis of environmental samples for PCBs was done by packed-column gas chromatography (GC). This is a low-resolution technique which allows the different Aroclors to be distinguished, but does not separate individual congeners. More recent analytical data has been obtained by high resolution capillary GC, which has far greater separating power (Figure 8). GC-MS is also becoming more common for determining PCBs as homolog groups (Slivon *et al.*, 1985; Alford-Stevens *et al.*, 1986).

The ability to carry out an analysis for individual PCBs is important. Chemical, physical, and toxicological properties vary substantially among the PCBs. Differences in volatility, water solubility, and reactivity often lead to PCB profiles in environmental samples that are markedly altered from those of the Aroclor fluids responsible for the contamination. Improvements in analytical techniques within the last 10-15 years has been critical to our current understanding of PCB environmental chemistry. Still, it is common for laboratories to include different numbers of congeners in their analytical scheme, making comparisons among research groups difficult. As is the case with PAHs, there has been a lack of standard reference materials (SRMs) for PCBs. Recently marine sediment SRMs for PCBs have become available through NIST and the National Research Council of Canada (Schantz *et al.*, 1990).

As is the case of PCDDFs, PCB profiles are greatly altered between source and receptor. This is largely due to the selective phase partitioning that is a consequence of the wide variation in physicochemical properties of individual PCB congeners. An example of the difference between PCB profiles in air and rain is shown in Figure 9 (Duinker and Bouchertall, 1989). PCBs in rain obviously originate from washout of the particle-bound, rather than the vapor-phase, PCBs in air. Further changes in profiles accompany sedimentation and bioaccumulation processes.

Schwartz *et al.* (1987) discussed the problem of quantifying PCBs as Aroclor mixture equivalents vs. as the sum of individual congeners. The conclusion was that samples should be analyzed for individual congeners, and total PCBs should be reported as their sum.

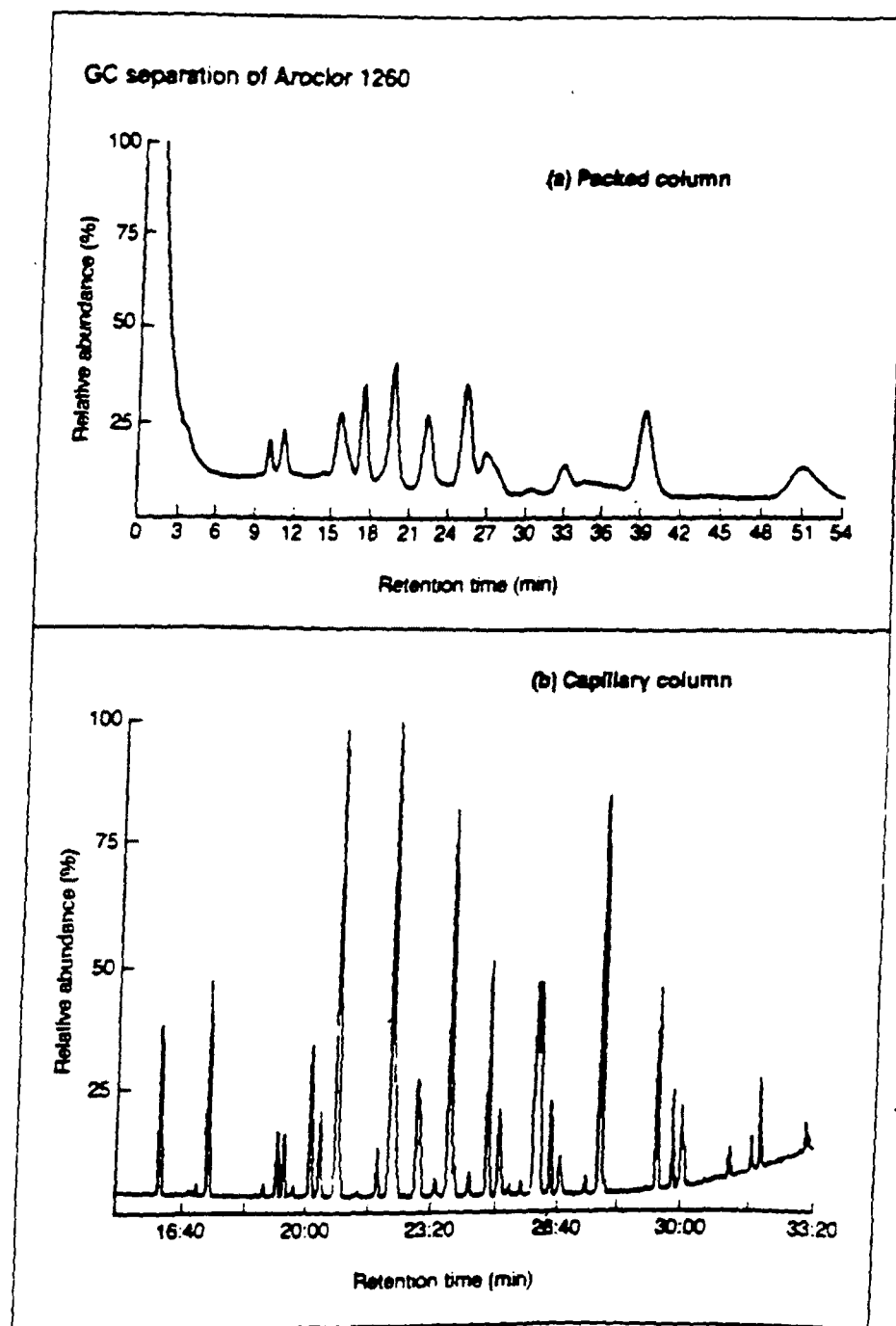
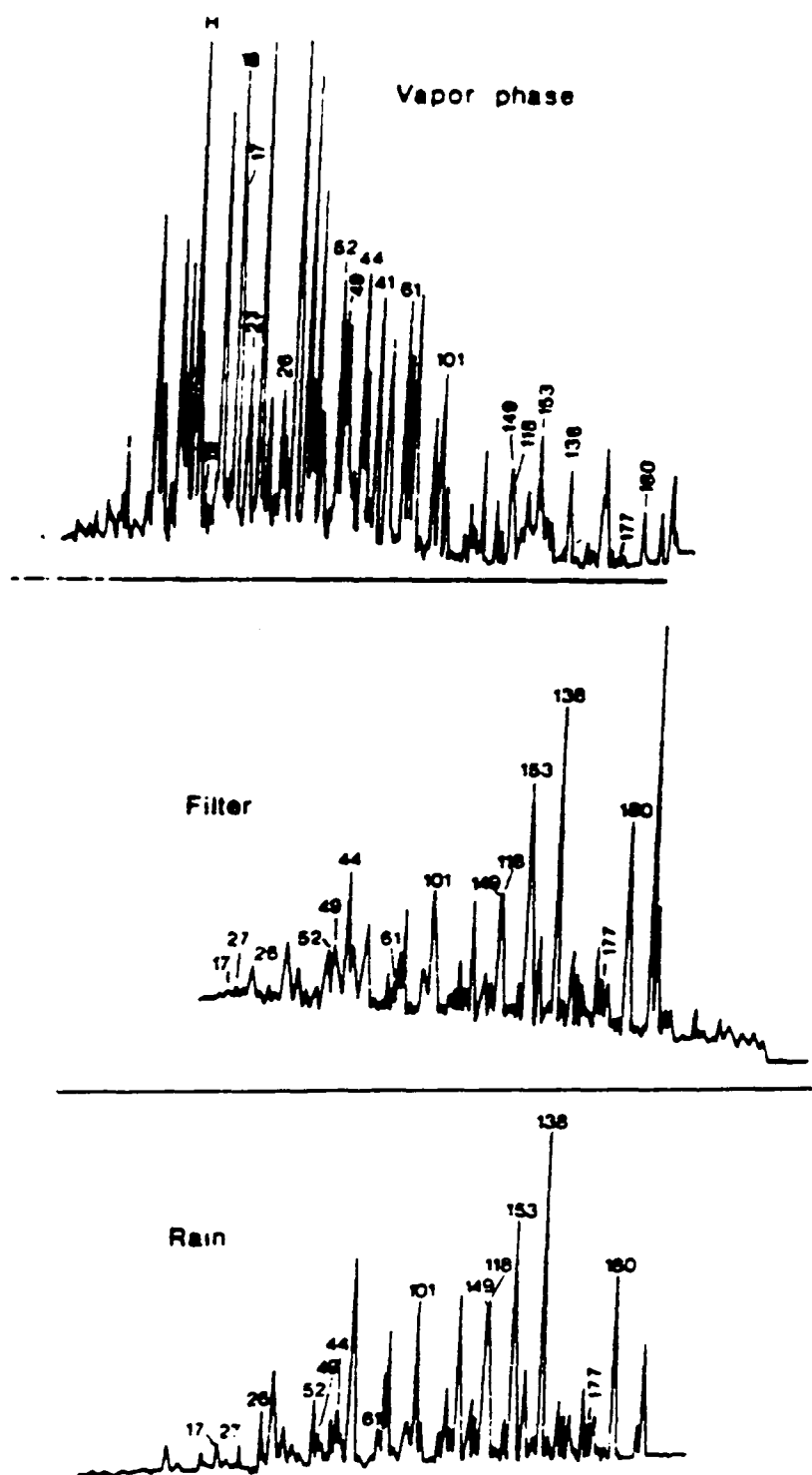


Figure 8. Comparison of packed and capillary-column gas chromatography for separating components of Aroclor 1260. Source Alford-Stevens (1986).



**Figure 9.** Profiles of PCBs in the particulate (filter) and vapor phases of ambient air, and in rain. Source: Duinker and Bouchertall (1992).

Little is known about the relative proportion of PCBs from different sources. Aroclor fluid compositions have been well established (Schulz *et al.*, 1989), but seldom have emissions profiles been established. Thus it is difficult to determine the origin of PCBs in an ambient air sample.

Profiles of PCBs in ambient air have been used to suggest sources in South Chicago. Murphy *et al.* (1985) noted that PCB patterns from most incinerators tested were similar to Aroclors 1248 or 1254. However one sewage sludge incinerator showed a predominance of heavy PCBs, similar to Aroclor 1260. Holsen *et al.* (1991) found that PCBs in two spring air samples from Chicago matched Aroclor 1260, while a third was similar to Aroclor 1242, a lighter PCB mixture. A series of air samples from South Chicago in February, 1989 showed great differences in absolute concentrations of PCBs and their profiles (Cotham, 1990). Profiles of most samples were skewed toward the low molecular weight PCBs, as is typical of ambient air. For these, total PCBs ranged from 300-2500 pg/m<sup>3</sup>. Two samples contained total PCBs of 4700 and 10,000 pg/m<sup>3</sup>, and were dominated by heavy components, as is Aroclor 1260. Thus three separate observations have documented that certain events in Chicago lead to distinct profiles of heavy PCBs in ambient air.

Several investigations have shown that PCBs volatilize from the Great Lakes and are a significant source to the atmosphere above the water (Achman and Eisenreich, 1992; Baker and Eisenreich, 1990; Hornbuckle *et al.*, 1992). Differences in PCB profiles over land and over the lake may be valuable in distinguishing freshly transported PCBs from those being recycled into the atmosphere from the lake (Hornbuckle *et al.*, 1992).

#### 4. IDENTIFICATION OF LOCAL SOURCES

The first step in defining the contribution of emissions from a given source or source region to the pollution load at a given receptor is to prepare chemical and physical characterization of this source/source region. This information is being prepared for the Great Lakes region through several research projects sponsored by the EPA, the Ontario Ministry of the Environment, and the International Joint Commission. A number of institutions have been involved in these projects and as a result several technical reports are now becoming available. The above described emission inventorying has been done mostly for precursors of atmospheric acid compounds, such as sulfur and nitrogen compounds, as well as some photochemical oxidants, such as selected volatile organic compounds. The hazardous pollutants, as defined in the 1990 Clean Air Act Amendments (CAAA), have been less well defined with respect to their emissions but this trend may be changing.

Two major conclusions can be drawn on the basis of current work on emission inventorying for toxic compounds. First, a list of source categories and processes generating emissions of hazardous air pollutants can and should be defined for the regions of interest. The above can be done for point and area sources, separately. The second conclusion is that ongoing work on inventorying emissions of criteria pollutants and VOCs, particularly those efforts that are based upon emissions inventories prepared under the National Acid Precipitation Assessment Program (NAPAP) should utilize point sources listing to estimate the emissions of toxic compounds as well as the criteria pollutants, e.g. electric power plants, smelters, incinerators, cement kilns, and chemical plants. This information is needed when preparing spatial distribution of toxic compound emissions within the study area.

#### **4.1. Major source categories for toxic compound emissions**

As pursuant to the requirements of the CAAA of 1990 an interim toxic emission inventory has been developed for the continental United States. Preliminary results of this work which includes the geographical distribution and source type analysis has recently been presented by Benjey and Coventry (1992). Several heavy metals were inventoried including arsenic, cadmium, lead and mercury which are of primary interest in this study. Altogether emissions of 28 compounds, both heavy metals and persistent organic pollutants have been inventoried based on the 1985 NAPAP inventory.

Toxic emissions in the Great Lakes region were also inventoried within other programs, such as the EPA Region V Project on Air Toxics Emission Inventories for the Lake Michigan Region, and other organizations, such as the International Joint Commission (IJC). The IJC report provides data on the production, usage and atmospheric emissions of 14 toxic chemicals, including the four heavy metals studied in this work, and other priority compounds: polynuclear aromatic hydrocarbons (PAH), dioxins, furans, polychlorinated biphenyls (PCBs), and pesticides, with a focus on lindane. More recently, an emission inventory for toxic compounds has been prepared within a project from the Ontario Ministry of the Environment.

An emission inventory of toxic air contaminants for the Great Lakes states is now being developed at the Michigan Department of Environmental Protection (Vial, 1992). When this work is completed it will be one of the most important sources of information on emissions in the Great Lake Region to date.

EPA is currently developing the Air Toxics Emission Inventory Protocol for the Great Lakes States (e.g. Radian, 1992). The Emission Inventory Branch in the EPA Office of Air

Quality Planning and Standards has recently prepared the Air Clearinghouse for Inventories and Emission Factors (AIR CHIEF) providing information on estimating air emissions of criteria and toxic pollutants from selected sources.

Preliminary results of the emission inventory for heavy metals in the United States, summarized by Benjey and Coventry (1992) suggest that the toxic metal emission sources are heavily influenced by primary and secondary metal production (93% of the arsenic emissions and more than 83% of the cadmium emissions), gasoline combustion (about 59% of the lead emissions) and waste incineration (more than 57% of the mercury emissions). The above emissions inventory is presently being revised and the relative contributions from the various source categories may change, particularly the importance of lead from gasoline combustion. Most of the emission sources for the above compounds are located outside the Great Lakes region according to this inventory, and mainly in Arizona for arsenic, and Missouri for cadmium. Emissions of lead and mercury are more evenly distributed. It should be admitted, however, that the above suggested source category contribution to the total emissions in the United States is somewhat surprising. Taking into account similarities in production technologies and efficiency of control equipment, as well as the chemical composition of wastes to be incinerated in the United States and Western Europe (e.g. Pacyna and Munch, 1988) one should modify a list of major source categories contributing to the atmospheric emissions of toxic metals in the United States.

Major source categories for emissions of toxic heavy metals and persistent organic compounds in the Great Waters regions include:

- combustion of bituminous coal, mostly in pulverized coal dry boilers, lignite, distillate oil, residual oil, and natural gas to produce electricity (emissions of all heavy metals of concern and PAH., dioxins, and furans),
- combustion of bituminous coal, distillate and residual oil, and natural gas in industrial boilers (emissions of pollutants as above),
- cement production in both dry and wet process kilns (emissions of heavy metals and PAH),
- production of chloro-alkali using Hg-cell (emissions of mercury),
- coke production as by-product in primary iron and steel manufacturing (emissions of all compounds except lindane),
- secondary non-ferrous metal (and mostly lead) production (emissions of heavy metals and PCBs),
- petroleum refineries (PAH),
- refineries and chemical industry (and particularly production of chlorine and caustic soda,

production of batteries, production of pigments, use of paint),

- paper and pulp production ( mostly emissions of PCBs),
- waste incineration ( emissions of all compounds except lindane),
- glass industry,
- production of fertilizers,
- crematories,
- combustion of fuels in internal engines ( emissions of lead, PAH, and dioxins),
- use of lindane in livestock treatment ( emissions of lindane), and
- use of lindane in wood and seed applications ( emissions of lindane).

Other source categories which emit large amounts of almost all of the compounds of interest are so-called diffuse sources. These include:

- combustion of gasoline and other fuels in motor vehicles,
- volatilization of compounds from landfills, both flared and unflared
- re-emission from terrestrial and aquatic environments (mostly mercury), and
- combustion of wood and other fuels to produce heat.

Impurities found in such products as pesticides, rubber tires, pigments and coatings can also become important local sources of toxic substances (Ayers, 1987).

Emissions of heavy metals from natural sources may also be quite important. However, as suggested by Lindqvist and Rodhe (1985) for mercury, it is perhaps misleading to categorize present day fluxes of mercury from soils, bodies of water, and biota as being "natural emissions". For example, past anthropogenic Hg emissions have been dispersed so thoroughly through the environment that this distinction is probably no longer meaningful. The flux of mercury to and from land and water surfaces has only recently been studied in any meaningful way (Schroeder *et al.*, 1992; Vandal *et al.*, 1991). These recent studies have emphasized the importance of the air-water exchange of mercury and its importance in the behavior and fate of mercury in the environment. In addition, we have a very poor understanding of the forms of mercury emitted from these "natural systems", but this is the focus of ongoing research (Fitzgerald *et al.*, 1991; Pacyna *et al.*, 1992). Natural sources which are of major importance include:

- re-emission of volatilized heavy metals from soil and surface waters,
- re-suspension of soil particles,
- forest fires, and
- volcanic eruptions.

Potential sources for the critical organic compounds studied in this work are vast. Some of the major source categories include:

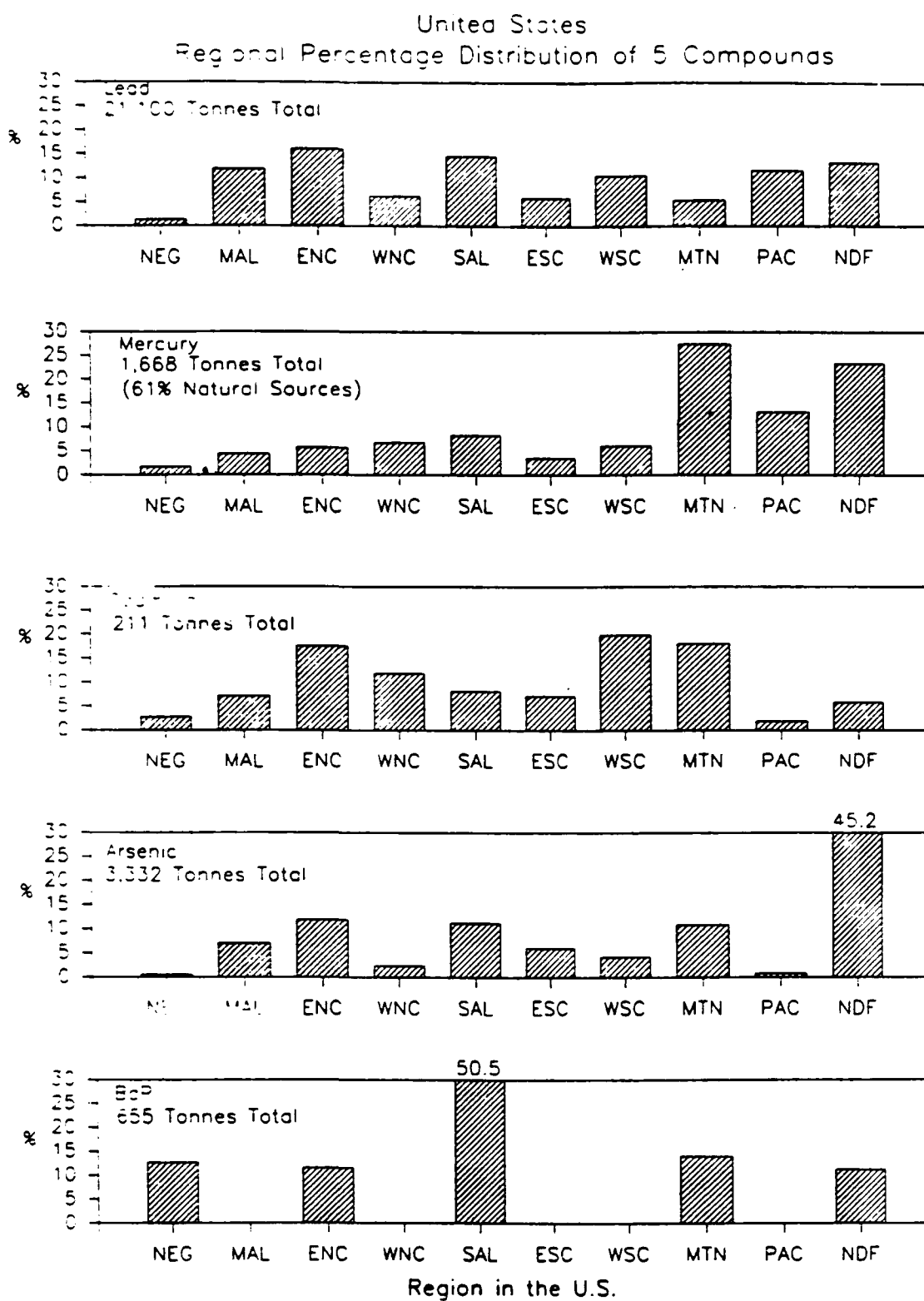
- application of pesticides,
- combustion of fossil fuels in electric power, co-generation and heat production plants,
- combustion of fossil fuels in commercial, industrial, and residential units,
- mobile sources,
- manufacturing and use of basic organic chemicals, and
- waste incineration.

Emission data currently reported by EPA and IJC, reveal that large portion of the emissions of toxic pollutants to the air in the United States can be generated outside the Great Lakes region. This is particularly true for emissions from point sources. However, the neighboring states, and particularly Missouri, generate large quantities of these emissions in electricity and heat producing power plants, primary and secondary non-ferrous smelters, steel and iron manufacturing plants, and waste incinerators. The contribution of atmospheric emissions of toxic compounds generated in various regions of the United States is presented in Figure 10, together with the emissions from 12 regions in Canada. The data were prepared on the basis of research carried out for IJC by Voldner and Smith (1989). This report covers two U.S. regions, specified in Figure 10 as East North Central (ENC) and Middle Atlantic (MAL) and Ontario (ON) in Canada as far as the Great Lakes are concerned. The contributions of toxic air compounds studied in this work from sources within ENC and MAL to the total U.S. emissions are varying from about 10% for mercury to 27% for lead. The emissions in ON contribute about 25% to the total Canadian emissions with bigger contribution for arsenic (more than 40%). The MAL and New England (NEG) should be considered for the Lake Champlain. Emissions in NEG do not contribute significantly to the total U.S. emissions of the studied compounds except for benzo-a-pyrene (BaP - included in PAHs). However, emissions sources in Quebec generate the largest amounts of toxic pollutants in Canada, in addition to Ontario.

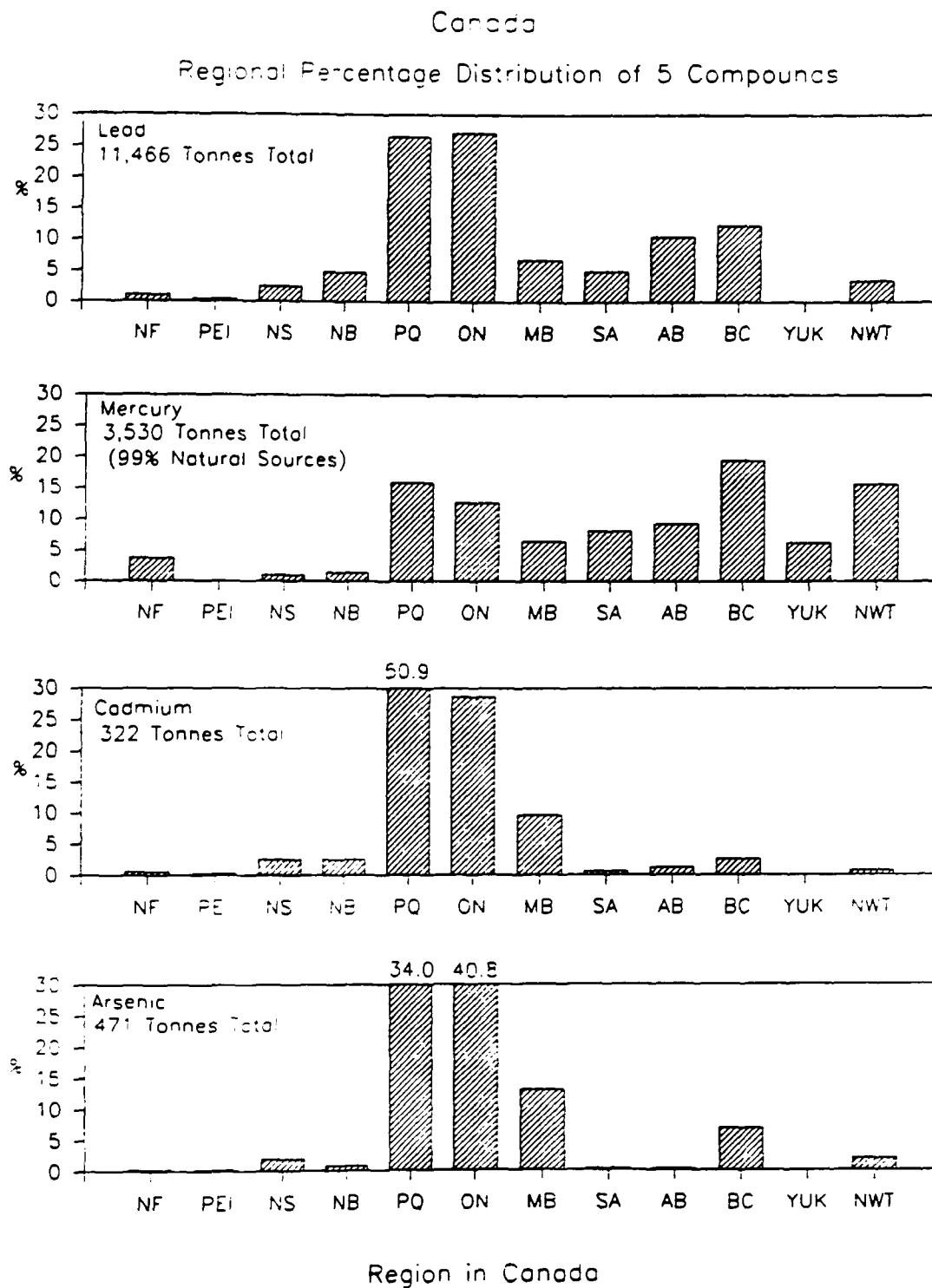
The emissions in SAL, having an impact on atmospheric deposition of toxic compounds onto the Chesapeake Bay waters, contribute between 10% and 15% to the total U.S. emissions of heavy metals, which is considered to be important. Even more significant is the contribution of persistent organic compounds reaching as much as 50% for BaP.

Although emitted in regions outside the Great Lakes, Lake Champlain, and the Chesapeake Bay, heavy metals and persistent organic compounds can reach the surface of these waters. Once emitted into the atmosphere, these pollutants are subject to long range transport.





**Figure10a.** Contribution of atmospheric emissions of selected toxic compounds from various regions to the total emissions in the United States.



**Figure10b.** Contribution of atmospheric emissions of selected toxic compounds from various regions to the total emissions in Canada.

during which transformations and deposition processes are occurring. The extent to which these processes take place depends upon stack parameters such as temperature and velocity of exhaust gases, meteorological conditions, and the physical and chemical forms of pollutants. The results from recent studies in Europe provide some basis for estimating what part of the heavy metals and organic compounds emitted from major point sources is deposited in the area of their emission sources (local deposition) and what part is transported and deposited outside the emission region.

In the case of emissions from point sources with a stack height of  $> 150$  m (e.g. large power plants, primary non-ferrous smelters, cement kilns, steel and iron plants and waste incinerators), all of which employ high temperature processes, only 15 to 20% of toxic emissions were deposited locally. The rest was transported out of the emission region. Less information on this subject is available from research in North America, however development of regional models in the area of the Great waters (e.g. Clark, 1992) would require data on local deposition. It is certain that we must consider emission sources both within the Great Waters region and outside the watersheds in order to assess the origin of atmospheric toxic compounds deposited on the water surface in the region.

The quantity of emissions for the heavy metals and persistent organic compounds of concern in the states around the Great Lakes, Lake Champlain, and the Chesapeake Bay is difficult to assess due to diversity of emission numbers reported by various research groups. The emissions estimates reviewed for this report differed by one order of magnitude, for most of the heavy metals considered in this, and are presently under revision and modification.

In order to revise the emission data more information is required on emissions within major source categories. Most of the work in this respect has been done for mercury. The emission quantities of mercury within major source categories in the Great Lakes region are given in Figure 11. Emissions of mercury during combustion of coal are clearly the highest, followed by emissions from waste incineration. Therefore, coal-fired power plants and waste incinerators in New York, Ohio, and Pennsylvania dominate emissions in the region. To prove this hypothesis, emissions of  $\text{SO}_2$  and total suspended particles (TSP) have been studied and results are shown in Figure 12. It can be noted that the  $\text{SO}_2$  emissions in Ohio alone contribute more than 11% to the total U.S. emissions of this compound and are followed by emissions in Pennsylvania. More even in the contribution of TSP emissions in the states around the Great Lakes to the total U.S. emissions of TSP. It should be noted that total suspended particulates are the major carrier of atmospheric heavy metals. The difference between the distribution pattern of  $\text{SO}_2$  and TSP emissions as shown in Figure 12 is mainly due to larger variety of sources emitting TSP compared to  $\text{SO}_2$ . The sources of the latter compound are more homogeneous. Even distribution of TSP

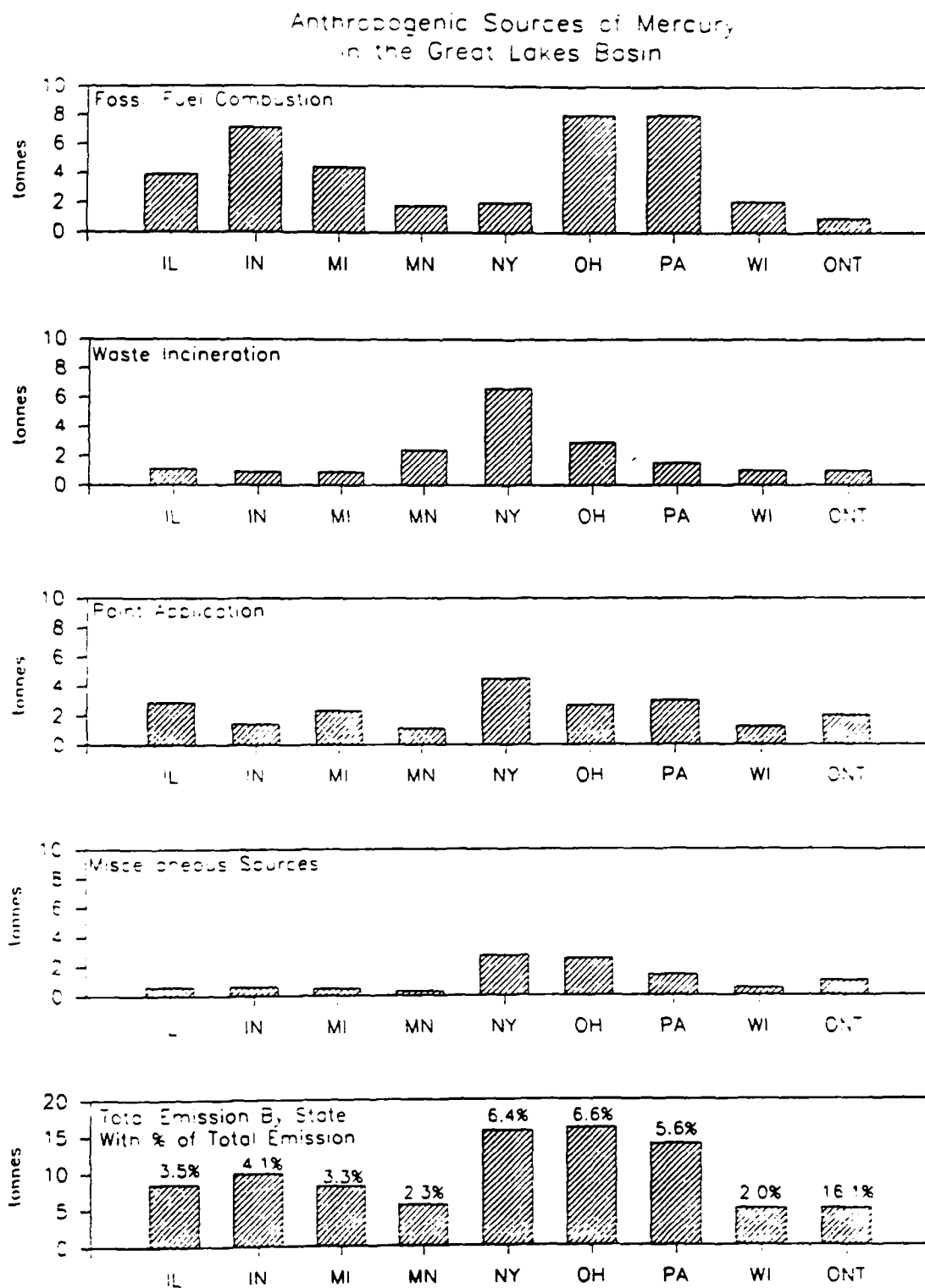
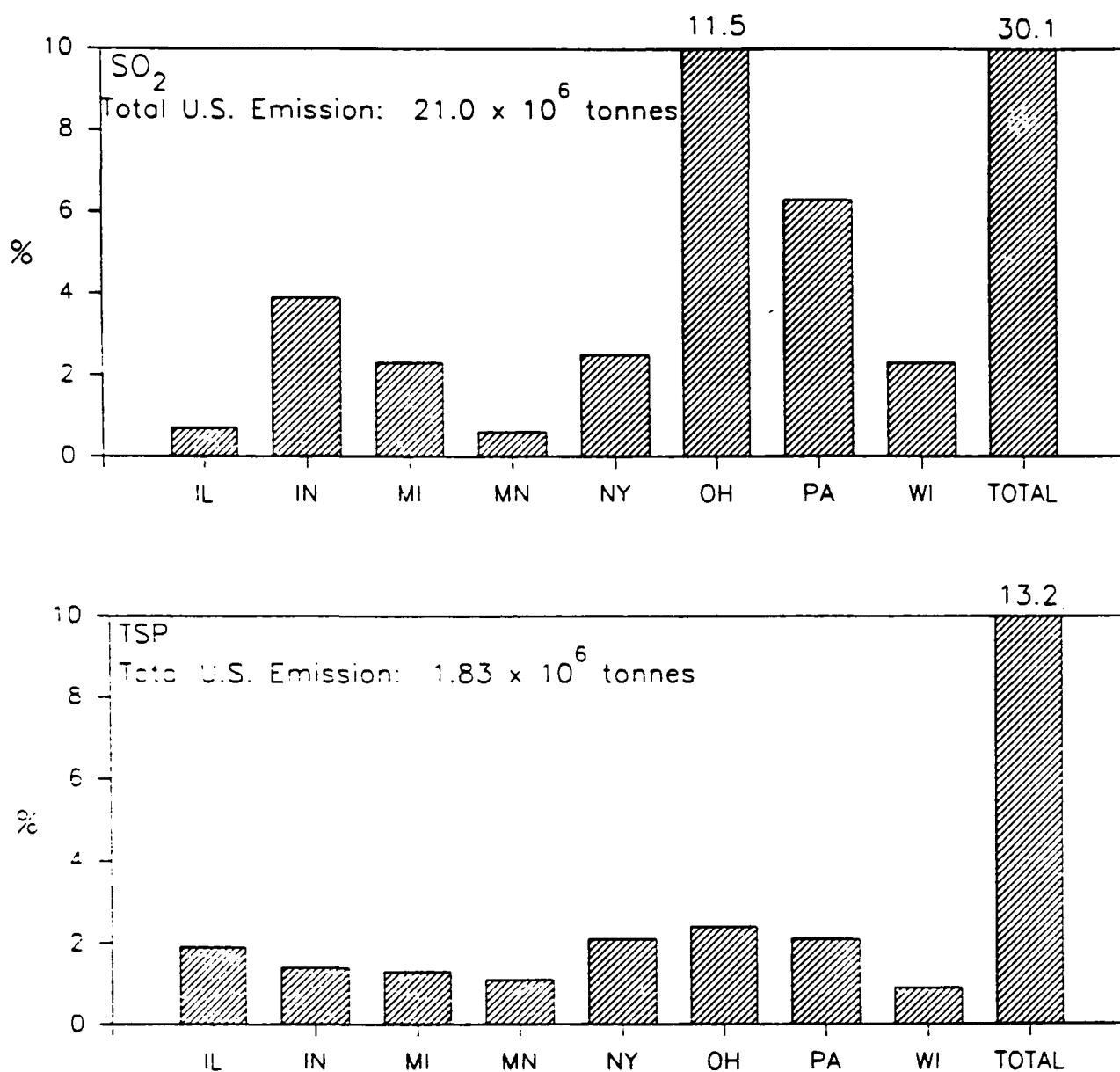


Figure 11. Contribution of atmospheric emissions of mercury from various source categories to the state emissions in the Great Lakes region.

PERCENTAGE CONTRIBUTION OF THE GREAT LAKE STATES TO  
THE TOTAL EMISSION OF SO<sub>2</sub> & TSP



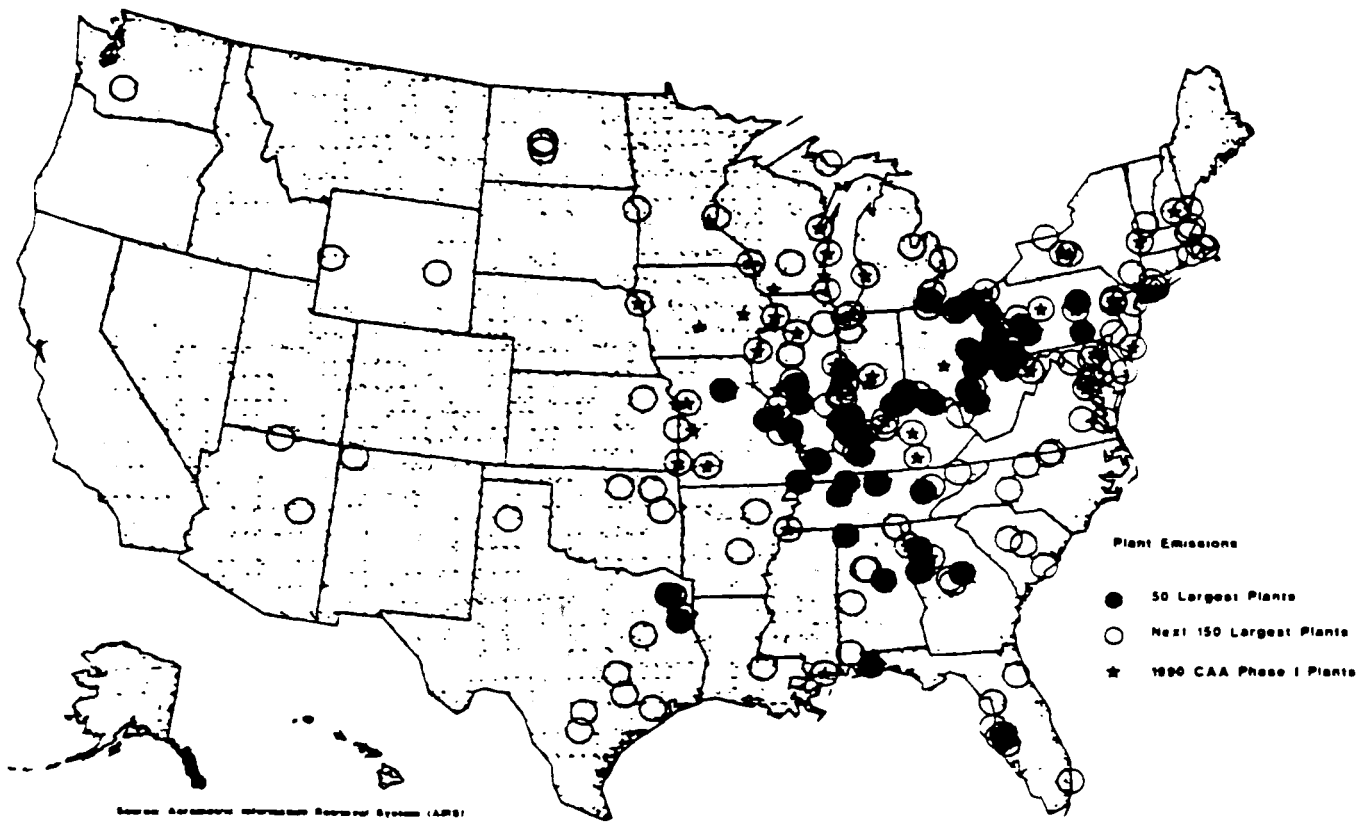
**Figure 12.** Contribution of emissions in the Great Lakes states to the total emissions of SO<sub>2</sub> and total suspended particles (TSP) in the United States.

emissions indicates that sources, such as waste incinerators, ferrous and non-ferrous smelters, and cement kilns located all-around the U.S., as well as area sources such as heat production and paint application (see even distribution of the Hg emissions from the latter source in Figure 11) can substantially contribute to the atmospheric deposition of the studied pollutants to the Great Lakes, Lake Champlain, and the Chesapeake Bay. It is, however, difficult to substantiate quantitatively the above suggestion due to a lack of information on source receptor relationships for the studied compounds, and particularly for the Chesapeake Bay and Lake Champlain. Although the measurements at receptors are sometime available, there is a chronic lack of emission data to study these relationships.

In the evaluation of the impact of emissions from local sources on deposition of pollutants into the Great Lakes, Chesapeake Bay and Lake Champlain, the locations of the largest point sources should be considered. If we first look at the location of the 200 largest power plant emitters of sulfur oxides (presented in Figure 13, EPA, 1991), most of the 50 largest plants are found in a belt from Missouri through Illinois, Indiana, Michigan, Ohio, West Virginia, to Pennsylvania. The contribution of the power plants in these states relative to the total power plant emissions for As, Cd, and Pb are shown in Figure 14. The plant design, and particularly the burner configuration, influences the emissions of trace metals (Pacyna, 1989). Wet bottom boilers generate the highest emissions among the coal-fired utility boilers because of the need to operate above the ash-melting temperature. At a typical peak temperature of about 1550 °C the volatile trace elements in the coal ash evaporate (Pacyna, 1980). Later they condense as submicron aerosol particles, or on the surface of ash particles as the flue gas cools to 370 - 450 °C in the convective heat transfer sections of the power plant. The emission rates from other types of boilers, such as wall-fired and tangential units seem to be lower due to the lower temperature involved. For mercury, however, the emissions do not differ as this element is volatile at low temperatures and passes the control equipment of electric-power stations almost entirely in the gas form.

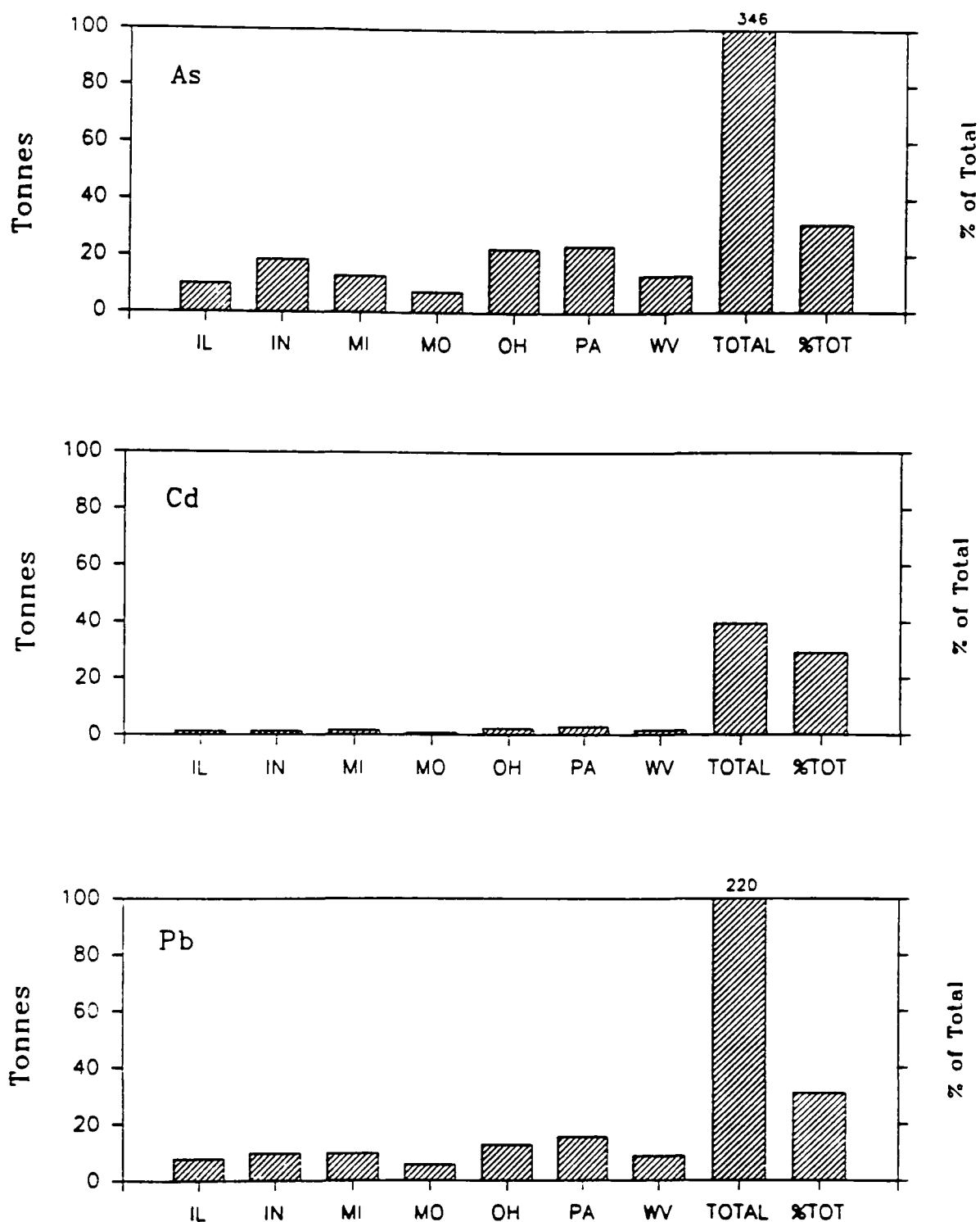
The remainder of the largest power plants in the United States are located mostly in the southern states; Texas, Tennessee, Alabama, Florida, and Georgia, as well as Kentucky. The next 150 largest power plants are more evenly located in the eastern and southern parts of the country with a higher density of plants in a few regions, including the region surrounding the Chesapeake Bay area. A fraction of the arsenic, cadmium, mercury, and lead emissions from the largest 200 power plants, and particularly those within the power plant belt as defined above, are probably deposited to the Great Lakes, the Chesapeake Bay waters, and also to the Lake Champlain basin. The latter region is probably also affected by emissions from combustion of fossil fuels in the

Quebec power plants. The degree of this impact is difficult to quantify on the basis of existing information on heavy metal emissions. However, results given in the NAPA report by Venkatram *et al.* (1990) indicate that nearly half of the sulfate wet deposition is due to sulfur emissions along the Ohio River Valley/Midwest region discussed above (See Figure 15).



**Figure13.** Location of 200 major power plants in the United States.

# Emission of Toxic Metals from Power Plants (1987)



**Figure 14.** Contribution of the As, Cd, and Pb emissions from power plants in Illinois, Indiana, Michigan, Missouri, Ohio, Pennsylvania, and West Virginia to the total emissions from power plants in the United States.



The location of major primary and secondary non-ferrous metal smelters was also reviewed because of the large emissions of atmospheric heavy metals from these plants, particularly those employing pyrometallurgical processes (Metal Bulletin Books - MBB, 1986). The major primary smelters are located outside the Great Waters study regions, with the exception of a copper smelter in the Upper Peninsula of Michigan, and their emissions impact on the Great waters is discussed later in this report. The type of technology employed in smelters, refineries, and other operations, such as roasting, has a major influence on the trace element emissions (Pacyna, 1989). Secondary smelters (International Lead and Zinc Study Group - ILZSG, 1984; 1985) are located in many areas in the U.S. However, their contribution to the atmospheric deposition of heavy metals is much lower than the impact of primary smelters due to the difference in the raw materials used. On the other hand, secondary smelters are considered mainly as local emitters as they release exhaust gases through rather small stacks (20 to 50 m) in comparison with tall stacks (over 100 m) in primary smelters. Several secondary smelters in Indiana, Illinois, Pennsylvania, Ohio, Michigan, New York, and Ontario generate emissions of heavy metals to the atmosphere which are probably deposited in the same region, the Great Lakes Basin. The same would apply to the contamination of the Lake Champlain waters by atmospheric emissions from secondary smelters in New York and Quebec, as well as the contamination of the Chesapeake Bay waters by emissions from smelters located in Maryland and West Virginia.

Another major point source for many of the compounds discussed in this report is sewage sludge incinerators. The density of sewage sludge incinerators is greatest in the eastern United States as shown in Figure 16.

## VOCs

A great deal of work has been put into developing inventories and characterizing the source profiles of different VOC emitters. In the U.S. VOCs are mainly anthropogenic; an inventory of biogenic non-methane hydrocarbons revealed that quantities released were 20 times lower than those from human activities (Lamb *et al.*, 1987). The 1985 NAPAP survey (Saeger *et al.*, 1989) identified over 3000 individual point and area source types for VOCs and included over 600 individual compounds. Piccot *et al.* (1992) expanded this to a global inventory of VOCs from anthropogenic sources by assuming that NAPAP data were representative of similar source types from around the world. Results showed that the U.S. leads the world in emissions of paraffins, aromatics, formaldehyde and other aldehydes, and marginally reactive compounds; accounting for 23 - 38% of the global total in each of these categories (Table 6). Emissions of most VOCs are highest in the eastern third of the country, including the Great Lakes and mid-

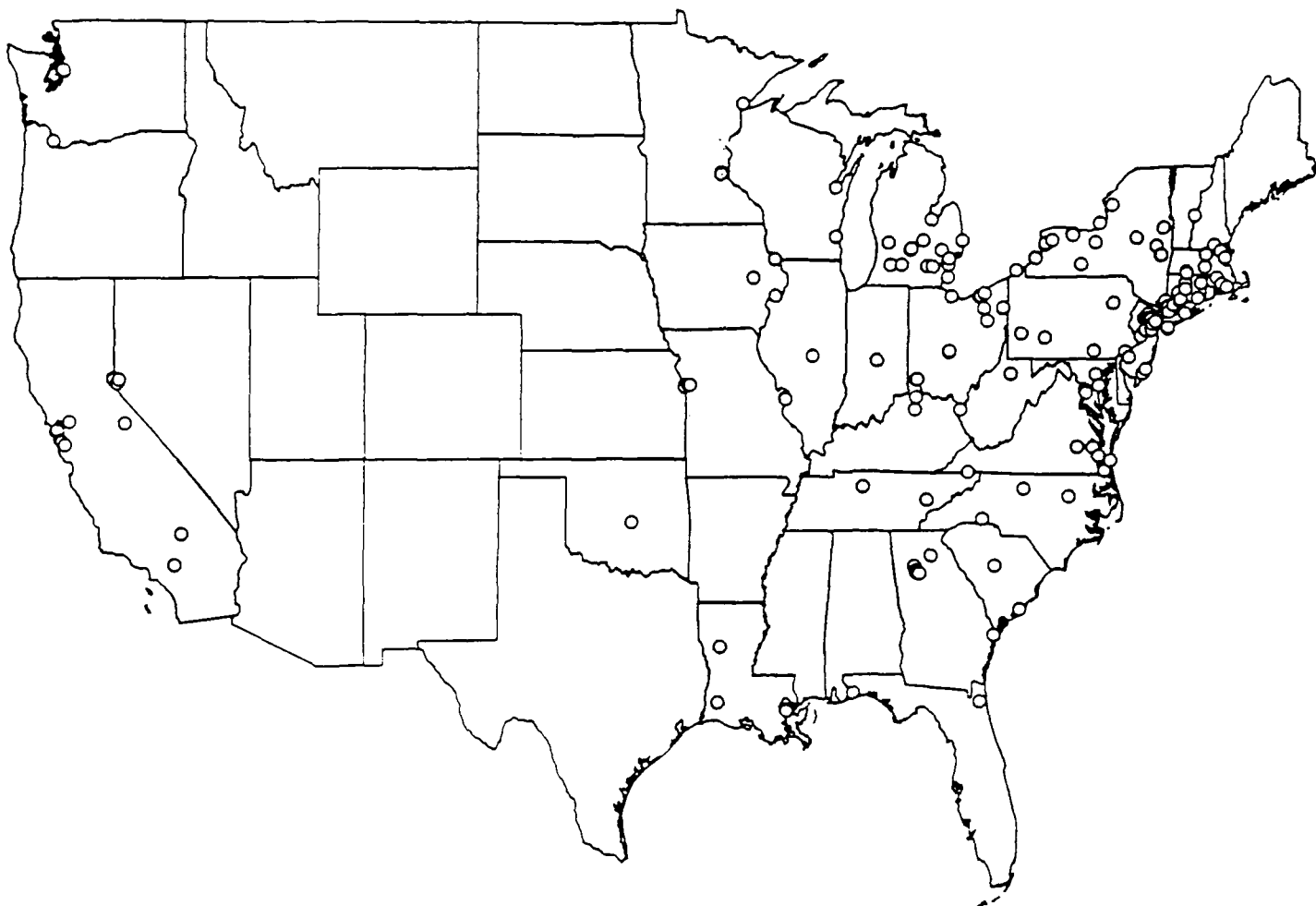


TABLE 6. Global and United States Emissions of VOCs,  $10^9$ g/y

	<u>World</u>	<u>U.S.A.</u>	<u>% of World</u>
Paraffins <sup>a</sup>	50258	11785	23.4
Olefins	38264	2772	7.2
BTX Aromatics <sup>b</sup>	14041	2534	18.0
Other Aromatics	4666	1750	37.5
Formaldehyde	1019	304	29.8
Other Aldehydes	307	102	33.2
Marginally Reactive <sup>c</sup>	910	264	29.0
Total	109465	19511	17.8

Source: Piccot et al., 1992.

- a) Includes straight- and branched-chain alkanes, alcohols, esters, and ketones.
- b) Benzene, toluene, xylenes.
- c) Includes most chlorinated and fluorinated compounds.



**Figure 16.** Location of major sewage sludge incinerators in the United States.  
Source: EPA Document 450/2-90-009 (1990).

Atlantic regions (Figure 17). The heaviest contributors of olefins are tropical Africa and Central and South America, the result of continental-scale biomass burning.

The Lake Michigan emissions survey by Blakley and Klevs (1990) speciated 1985 NEDs/NAPAP total VOCs data and assigned releases of individual compounds on a gridded network. Over 100,000 tons of air toxics were emitted from point and mobile sources within a 21-county area surrounding the Lake Michigan Basin. Approximately 15,000 tons were emitted from point sources, of which over 90% were located in Illinois and Indiana. Releases from point sources are listed by facility and county. Benzene and light chlorinated compounds were major contributors to total VOCs from point sources, amounting to 5097 and 5548 tons/y. Highest releases of benzene occurred in four counties near the southern end of the lake: Will and Cook (Illinois), Lake and Porter (Indiana). The latter three counties were also listed as having substantial coke oven emissions. Following the point source presentation is a list of emissions from all sources (point + area) by grid within the 21 counties.

Prototype VOCs emission inventories were made for ten counties in southeast Virginia (Emmim *et al.*, 1989) and later expanded to eleven midwestern and mid-Atlantic states (Wind and Burke, 1990). The estimates were made from NEDS point source and area source data for VOCs, and in the case of the 11-state study, also from 1988 mileage data from the Federal Highway Administration. Total VOCs were speciated using apportionment factors provided by Radian Corporation. Atmospheric release of carcinogenic VOCs in the Virginia counties was estimated to be 1987 tons/y, broken down into: gasoline vapor 38.6%, benzene 21.7%, formaldehyde 21.0%, chlorinated solvents 10.0%, and acrylonitrile 8.6%. Vehicles accounted for about half the benzene released; the remainder was from point sources. For the eleven states, VOCs emitted totaled 813,400 tons/y. Vehicles accounted for 66.3% of the 333,200 tons of benzene + toluene released.

### PAHs

For PAHs, the relative importance of different sources changes seasonally and as society achieves greater control measures (Baek *et al.*, 1991a,b). For example, Harkov and Greenburg (1985) calculated that 183 kg BaP (98% of total) was released by motor vehicles in New Jersey during the non-heating season, but 6135 kg BaP (98% of total) reached the atmosphere through residential wood combustion during the heating season. A 5-10 fold drop in PAH levels in the Baltimore Harbor Tunnel between the mid-1970s and 1985-86 was attributed to installation of catalytic converters in the later years (Benner *et al.*, 1989). The drop in aerial BaP concentrations in the Great Lakes region over the last two decades has been accompanied by a decline in the BaP content of surface sediments in the lakes (Eadie, 1984; Eadie *et al.*, 1990).

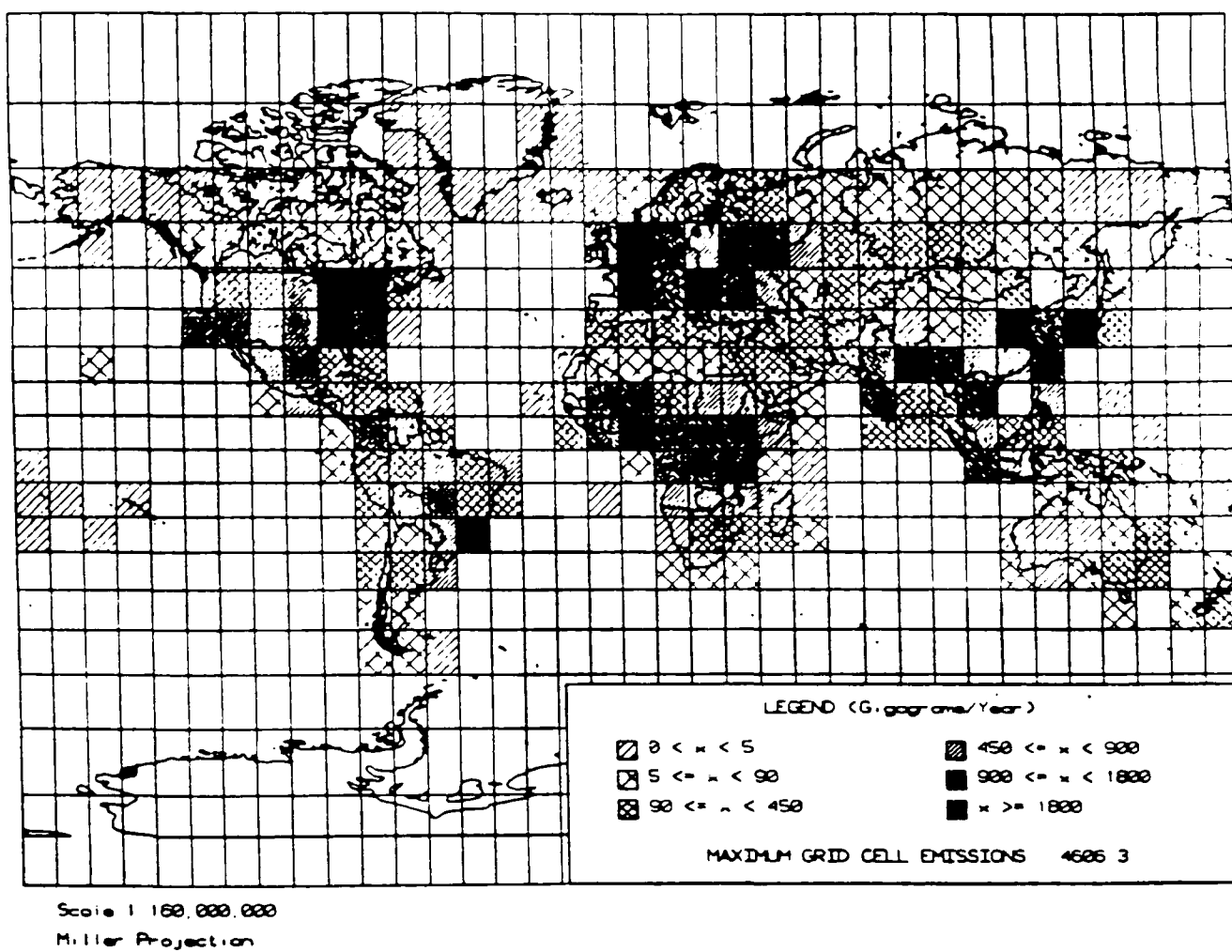


Figure 17. Global distribution of total VOCs,  $10^9$  g/y. Source: Piccot *et al.*, 1992.

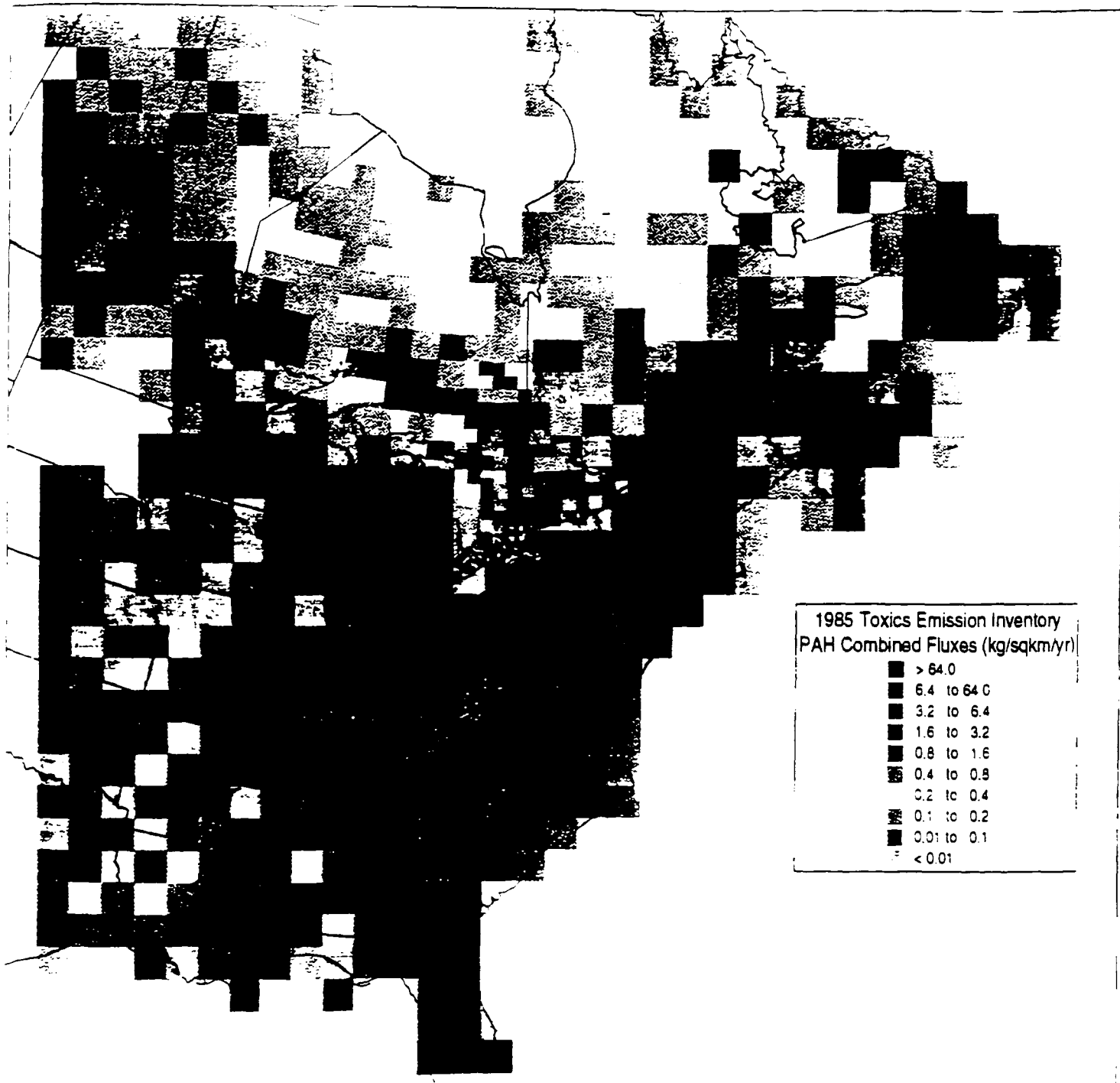
One of the most detailed studies on emissions of these pollutants and their spatial distribution around the Great Lakes has been carried out for the Ontario Ministry of the Environment (Johnson *et al.*, 1990). Spatial distributions of the annual emissions of PAH, PCDD, PCDF, and insecticides in Eastern North America within 127 km x 127 km polar stereographic grid system are presented in Figures 18-21, respectively.

A great deal of effort was made to compile or estimate PAH emission factors for a large number of source types, including industrial processes, vehicles, residential combustion (wood, coal and oil), power plants, incinerators, open prescribed burning, and forest fires.

One can note the large difference in emission factors among source types. For example those from industrial and utility coal combustion are given in mg/metric ton coal burned, whereas ferroalloy and aluminum production and residential wood stoves are in g/metric ton metal produced or fuel burned. Large differences in emissions and ratios among PAH compounds can be seen for vehicles with two types of catalysts.

The source-to-source variability within each of these categories is also quite large, typically an order of magnitude or more. Even within a particular industry, differences in a process can greatly change quantities of PAH released. For example, Johnson *et al.* (1990) total PAHs released by aluminum reduction facilities from 330 to 2,430 g/ metric ton aluminum produced, depending on whether the process is a pre-bake anode Soderberg or a horizontal Soderberg. PAHs released from metallurgical coke production were raised from 450 to 1300 mg/metric ton coal charged when partly contaminated water was used for coke quenching instead of clean water.

Annual releases of PAHs to the atmosphere totaled 272 metric tons in Ontario (ONT) and 9397 metric tons in eastern North America (ENA). These ranged in molecular weight from acenaphthylene (152) to coronene (300). Of total PAHs, 1.9% was estimated to be BaP in ONT and 3.6% in ENA. This difference was attributed to the greater variety of sources in ENA and their relative contribution to the total. Within Ontario, the largest emissions took place along the northern shores of lakes Ontario and Erie. Over ENA, PAH releases were largest in a wide diagonal extending across the midwestern states from southern Illinois to the mid-Atlantic and southern New England states. In this corridor, emission fluxes were 1.6 - 6.4 kg/km<sup>2</sup>-y, with an occasional grid showing higher values. Fluxes throughout the Appalachian region and the southeast were typically lower: 0.4 - 3.2 kg/km<sup>2</sup>-y, with "hot spots" found near southern cities.



**Figure 18.** Spatial distributions of annual emissions of PAH in Eastern North America within 127 km x 127 km polar stereographic grid system.



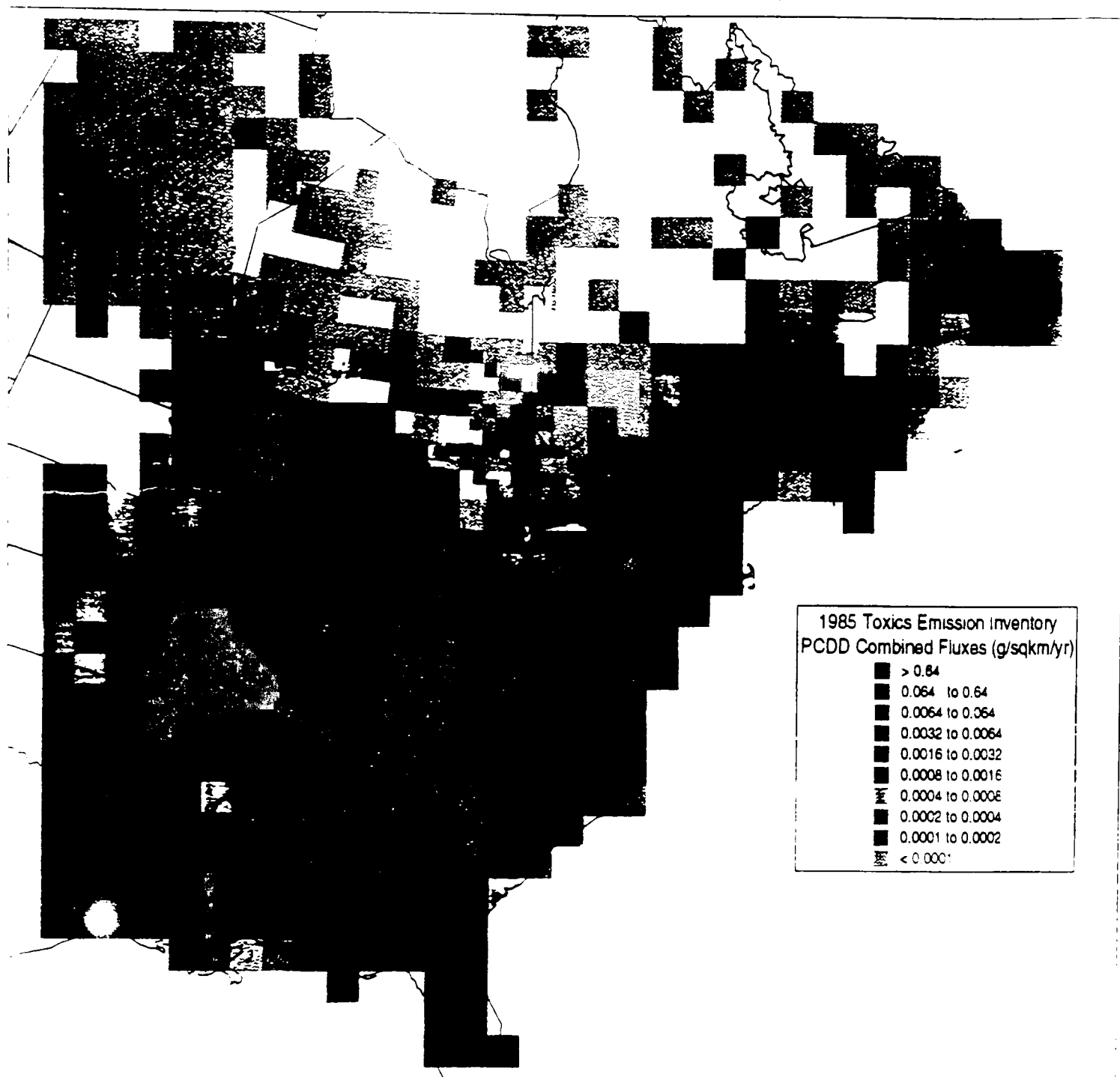
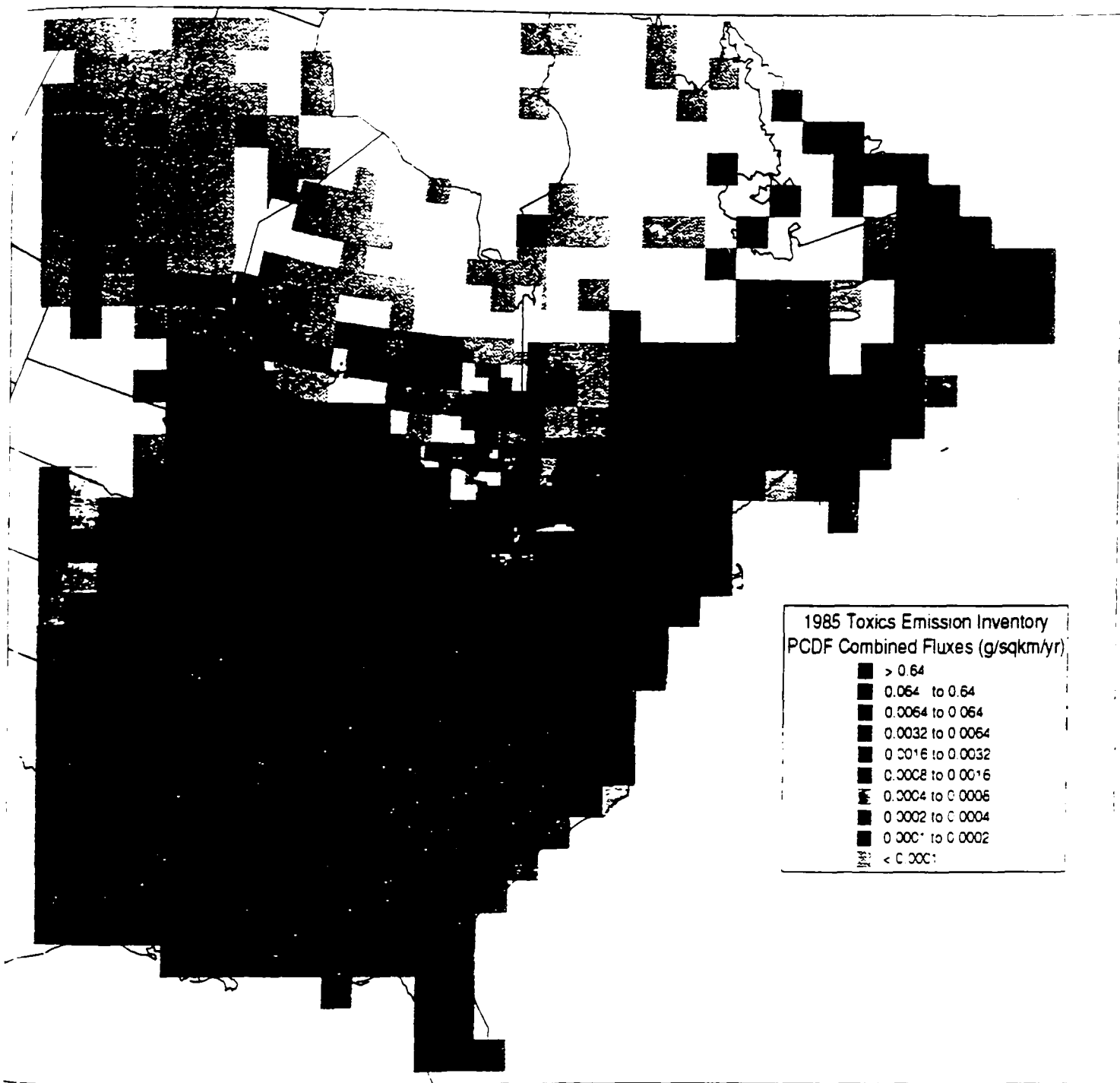
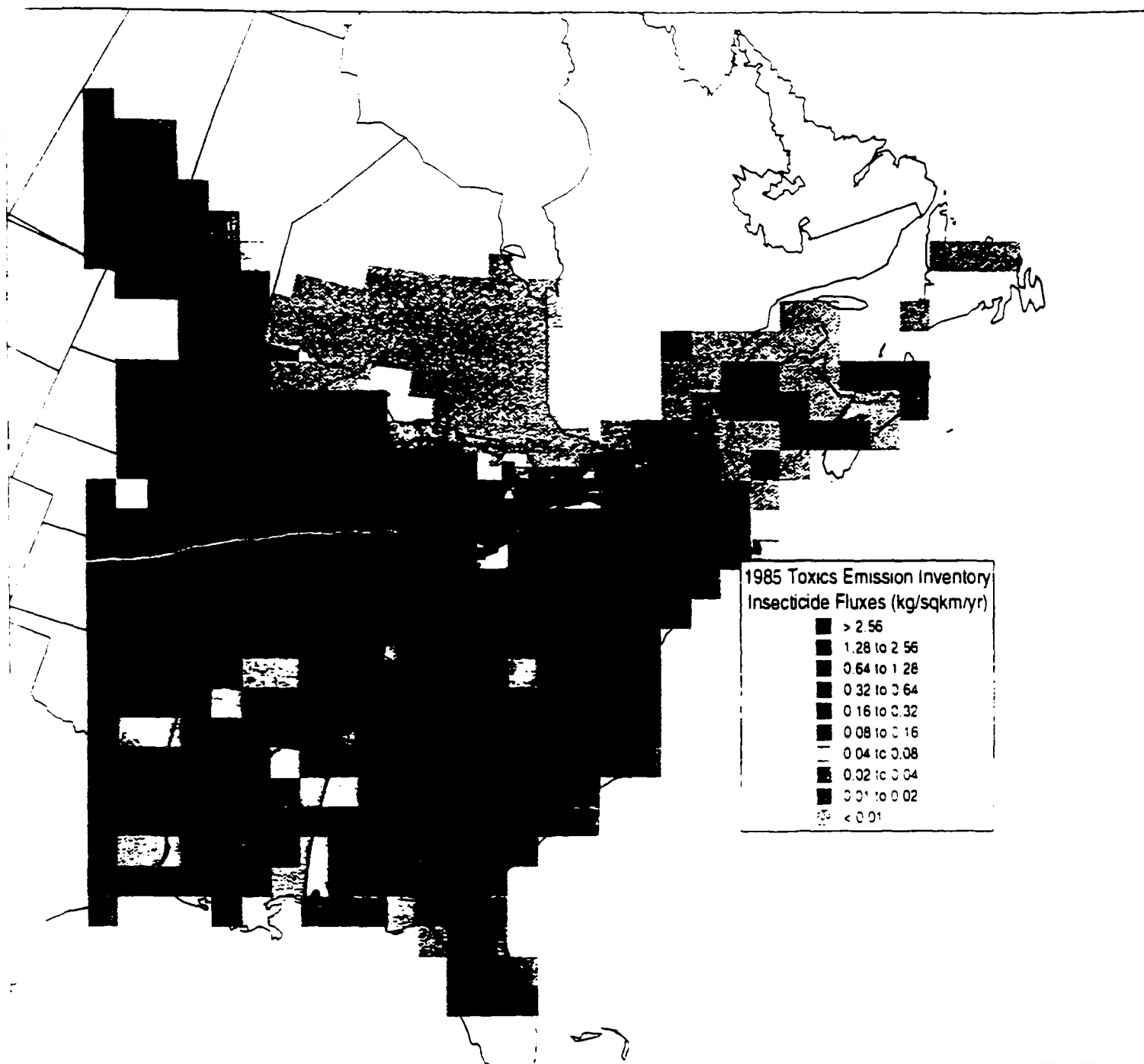


Figure 19. Spatial distributions of annual emissions of PCDD in Eastern North America within 127 km x 127 km polar stereographic grid system.



**Figure 20.** Spatial distributions of annual emissions of PCDF in Eastern North America within 127 km x 127 km polar stereographic grid system.



**Figure 21.** Spatial distributions of annual emissions of insecticides in Eastern North America within 127 km x 127 km polar stereographic grid system.

Table 7 gives PAH emissions by source class, and also compares the recent estimates of Johnson *et al.* (1992) with those from mid-1970s data by Peters (1981) and Ramdahl *et al.* (1983). A much more extensive breakdown of ONT and ENA emissions is given in the original Johnson report pp. 322, 323, and 330-333. For example, 10 types of production facilities are listed under the "Industrial" category. "Stationary Fuel Combustion" is divided into commercial and residential fuel and wood combustion, and electric power generation. Contributions of on- and off-road gasoline and diesel vehicles, aircraft, railroad, and marine vessels are listed under "Transportation". Residential wood combustion dominated emissions, accounting for 51% of total PAHs in ONT and 31% in ENA.

TABLE 7. Atmospheric Emissions of PAHs by Source Class, Tonnes/y

	Ontario	Eastern N. America	Eastern U.S.A.	Total A	U.S.A. B
Industrial	82.3	2,704	1,831	640	3,497
Stationary fuel combustion	155.0	4,545	3,882	4,044	1,781
Solid waste incineration	0.7	48.5	<73	56	50
Transportation	24.5	1,174	1,099	2,266	2,170
Open Sources	9.2	926	440	4,025	4,100
Total	271.7	9,397	7,325	11,031	8,598

Sources: Johnson *et al.* (1992, p. 321) for all but A and B. Based on 1985 data.

A = Peters *et al.*, 1981; B = Ramdahl *et al.*, 1983; summarized by Baek *et al.* (1991, p.283). Based on mid-1970s data.

Emissions of BaP were estimated in 10 counties surrounding Lake Michigan by speciating 1985 NAPAP particulate matter data Blakley and Klevs (1990). Releases totaled 0.96 ton/y, of which 0.82 tons/y came from Porter County, Indiana.

Atmospheric emissions of BaP were estimated at 654 tons/y for the entire U.S. by Wilber *et al.* (1992) and Voldner and Smith (1989). The breakdown by source type was: 85.6% wood combustion, 6.1% agricultural burning, 3.1% wildfire, 2.0% vehicles, 1.4% coal combustion, 1.3% coke production, and 0.5% other sources. By comparison, the Johnson report estimated release to the atmosphere of 5.1 metric tons/y BaP in ONT and 340 metric tons/y in ENA.

A review of major power plants and aluminum smelters has been performed to investigate the impact of these plants on the contamination of the Great waters by PAHs. The power plants within the belt, as described earlier, emit large amounts of PAHs and their impact on the contamination of the Great Lakes and Chesapeake Bay waters is thought to be significant for heavy metals.

Major aluminum smelters in the U.S. are located in many locations in the country, including facilities in Indiana, Pennsylvania, Illinois, Ohio, and New York (MBB, 1986). Their impact on the contamination of the Great Lakes waters by PAHs is probably high. However, the impact is difficult to quantify due to the lack of emission data to be used in source-receptor studies. Smelters in Maryland should also be of concern when discussing the origin of PAHs in the Chesapeake Bay waters.

### **PCDDFs**

Voldner and Smith (1989) identified primary sources of PCDDs and PCDFs in Canada as being combustion of municipal and industrial waste, accidental fires of treated wood products, production spills during transportation and aerial spraying of herbicides, wood stoves, and PCB fires. Erickson (1989) concluded that PCB fires produce PCDFs, but not PCDDs. Secondary sources listed by Voldner and Smith were volatilization and erosion of dust from landfill sites and from areas where PCDDFs were present as impurities in herbicides. From the recent review by Johnson *et al.* (1992) the most important contributors of PCDDFs in ENA are incineration of industrial and municipal waste, residential and industrial wood combustion, and electric power generation. Secondary copper production (wire reclaiming) was listed as an important source in ONT.

Emission factors for some of the major source types are given in the Johnson *et al.* (1992) report. The authors stressed the high degree of variability and/or lack of emission factors for a number of processes.

Differences in PCDDF releases by incinerators are large, and depend on many variables. For example, emission factors for the municipal incinerators surveyed by Johnson ranged from 1 - 36 mg PCDDFs per metric ton of refuse burned. Edgerton *et al.* (1989b) reported total PCDD emissions from municipal incinerators ranging from 1 - 4259 ng per dry standard cubic meter air. Highest releases were from facilities operating under unsteady burning conditions.

A great number of incinerator surveys have been done, and relationships of PCDDF output to operating conditions have been evaluated. Many of these studies are published in the

annual symposia on "Chlorinated Dioxins and Related Compounds", *Chemosphere*, Vols. 19-23 (1989-91). Some of the important variables are: a) precursor content of the feed (e.g. presence of chlorine-containing species), b) type and extent of feed processing (e.g. removal of non-combustible material, shredding or pelletizing refuse), c) combustion and operating conditions (temperature, oxygen, residence time), d) type of incinerator and supplementary fuel, and f) type and efficiency of emission control devices (Johnson *et al.*, 1992).

PCDDF emissions in ONT and ENA as estimated by Johnson *et al.* (1992) are listed in Table 8 for different source categories. Stationary fuel combustion and solid waste incineration (municipal and industrial) were by far the dominant emitters. The fact that industrial emissions for ONT and ENA were nearly identical was explained by the fact that emission factors were available for only two industries -- secondary copper production and Kraft pulping, and that emissions for areas other than ONT could be underestimated for lack of point sources identification and base quantity information.

On the gridded map of ENA, emission fluxes of PCDDFs were remarkably uniform, falling between 6.4 - 64 mg/km<sup>2</sup>-y in most regions. Higher fluxes were generally associated with urban areas. North of the Great Lakes, fluxes dropped to <0.1 - 0.8 mg/km<sup>2</sup>-y, with an occasional hot spot.

TABLE 8. Atmospheric Emissions of PCDDs/PCDFs by Source Class, kg/y

	<u>Ontario</u>	<u>Eastern N. America</u>
Industrial	15.6	17.6
Stationary fuel combustion	8.62	190
Solid waste incineration	10.5	191
Transportation	0.1	8.46
Open Sources	0.016	6.57
Total	34.8	414

Sources: Johnson *et al.* (1992, p. 321) Based on 1985 data

## Pesticides

It has been very difficult to obtain reliable figures on the production and use of pesticides because of proprietary restrictions. Most OC insecticides have been banned in industrialized countries (exceptions in the U.S. and Canada are lindane, endo-sulfan, methoxychlor, and dicofol). Some historical usage data are available, and have been compiled by Voldner and Smith (1989). These and other figures taken from a U.S. EPA (1987c) report on termiticides are given in Table 9.

Many OC pesticides which have been banned in the U.S. and Canada continue to be used in Mexico, Central and South America, Africa, and Asia. Foreign production and usage information is extremely important for long-lived OC pesticides. A portion of these chemicals entering the Great Waters today could come from sources outside the U.S., or even North America.

Reliable statistics are very difficult to obtain, however reports to the Food and Agricultural Organization of the United Nations (FAO, 1986-89) show that Mexico used the following OCs in recent years (metric tons/y): DDT = 200-300, technical HCH = 180-250, lindane = 15-45, toxaphene = 600-1200. Toxaphene is manufactured in Nicaragua, and local contamination of human milk and foods has been found (Muller *et al.*, 1988). The FAO also reports heavy usage of OC pesticides in India, in excess of 20,000 metric tons technical HCH and 200-900 metric tons DDT per year. Information from the India Dept. of Chemicals & Petrochemicals (IDCP) (Spencer, 1991) indicates annual production of 25,000 - 28,000 metric tons of technical HCH between 1986-90, in agreement with FAO data. The IDCP gives far higher figures for DDT: 6700 - 8600 metric tons.

In 1989/90 Resources for the Future, Inc. (RFF) conducted a mail survey of U.S. Dept. of Agriculture Extension Service weed scientists to determine herbicide use for major crops. Replies were integrated with data from other surveys to form a national herbicide use database. The report (Gianessi and Puffer, 1990) summarizes applications of 50 chemicals on a state-by-state basis and by crop treated for 1987.

Table 10, taken from the RFF report summaries, shows the top ten herbicides used in the U.S. These accounted for 73% of herbicide use in 1987. Two-thirds of all herbicide in crop production were applied to corn and soybeans. Non-crop usage of these 10 chemicals was minor, with the exception of 2,4-D. The breakdown of totals herbicides by state and crop is given in

TABLE 9. Production, Sales or Usage of Some Organochlorine Pesticides in the U.S.A. and Canada, Metric tons/y.

<u>DDT, U.S.A.</u>		<u>DDT, Canada</u>		<u>Toxaphene, U.S.A.</u>	
1950-54	139,000	1968	831	1964-68	80,700
1955-59	160,000	1969	894	1969-73	100,700
1960-64	141,000	1970	287	1974-78	110,900
1965-69	90,000	1971	137	1979-83	24,730
1970-72	11,000			1984-85a	4,000

<u>Aldrin + Dieldrin, U.S.A.</u>		<u>Aldrin + Dieldrin, Canada</u>	
1950-54	5,750	1968	86
1955-59	17,640	1969	58
1960-64	30,100	1970	20
1965-69	37,730		
1970-73	20,200		
1981-85	2,270-3,400 <sup>b</sup>		

<u>Chlordane, U.S.A.<sup>b</sup></u>		<u>Heptachlor, U.S.A.<sup>b</sup></u>	
1980	4,300	1980	910
1985	1,450	1985	340
1986	1,800	1986	340

<u>Lindane, U.S.A.<sup>c</sup></u>		<u>Lindane, Canada</u>	
1964	617	1968	16
1966	312	1969	3
1971	269	1970	3
1974	1,600	1971	3
1975	2,900	1984	250
1976	13,100		
1977	152,000		

<u>Mirex-Dechlorane, U.S.A.</u>		<u>Mirex-Dechlorane, Canada</u>	
1959-63	187	1963	9.2
1964-68	934	1964	25.3
1969-73	344	1965	46.1
1974-75	61	1966	37.8
		1967	23.2
		1968	3.9

Sources: Voldner and Smith (1988), unless stated otherwise.

a) Production banned in 1982, but remaining stocks used until 1986.

b) U.S. EPA (1987b), 1981-85 aldrin/dieldrin figures are imports.

c) Imports from 1974-77. Large increase in 1977 probably due to ban of technical HCH in 1976.



Table 11. Corn- and wheat-growing states in the Midwest and Plains were the major targets for herbicides; Texas and California also ranked among the top ten users. Heaviest tonnages of herbicides were applied to corn, followed by soybeans.

TABLE 10. Top Ten Herbicides Used in 1987-89.

<b><u>Active Ingredients</u></b>	<b>Total Usage</b>	<b>% Share</b>
	<b><u>Metric Tons/Y</u></b>	<b><u>Corn/Soybeans</u></b>
Atrazine	29,090	84
Alachlor	25,000	91
Metolachlo	22,727	87
EPTC	17,818	79
2,4-D	15,000	12
Trifluralin	12,273	63
Cyanazine	10,455	90
Butylate	8,636	99
Pendimethalin	5,909	70
Glyphosate	5,454	44

Source: Gianessi and Puffer (1990, p. 7).

The National Oceanic and Atmospheric Administration (NOAA) maintains a data base for 35 herbicides, insecticides, and fungicides commonly applied in coastal watersheds. A report which is in the final stages of publication (Pait *et al.*, 1992) summarizes pesticide usage in estuarine drainage areas for 1987. This information was obtained from the RFF report and also from state data bases. The seasonality of pesticide application was assessed by surveys of representative counties within each coastal state. The information that follows is taken from the pre-publication version of the Pait report.

Over 13,363 metric tons of the 35 pesticides were applied in estuarine drainage areas. Of this, 69% were herbicides, 24% insecticides, and 7% fungicides. Alachlor and atrazine accounted for almost 45% of the total herbicides. By region, total pesticide use was divided as follows:

North Atlantic	0.8%
Middle Atlantic	27.0%

South Atlantic	33.5%
Gulf of Mexico	34.3%
Pacific	4.4%

The breakdown of total pesticides by drainage area is shown in Figure 22 (Pait *et al.*, 1992). Chesapeake Bay ranked first, followed Albemarle/Pamlico Sound in North Carolina and Winyah Bay in South Carolina.

**TABLE 11. States and Crops with Largest Annual Use of Herbicides.**

<b>State</b>	<b>Total Usage Metric Tons/Y</b>	<b>% Share Corn/Soybeans</b>
Iowa	20,909	96
Illinois	20,455	95
Minnesota	13,636	86
Texas	12,272	18
Indiana	11,364	97
Nebraska	10,000	84
Ohio	8,636	84
Kansas	8,182	43
Missouri	7,727	71
California	6,364	6

<b>Crop</b>	<b>Total Usage Metric Tons/Y</b>
Corn	93,636
Soybeans	37,273
Pasture	12,727
Cotton	11,818
Sorghum	10,000
Wheat	8,182
Rice	6,818
Alfalfa	3,182
Peanuts	2,273
Barley	2,272

Source: Gianessi and Puffer (1990, pp. 8 and 9).

Quantities and relative amounts of various pesticides changed with location. Figure 23 compares tonnages of 15 pesticides used in four of the above estuarine regions. The appendix of the Pait report contains quantities of each pesticides applied in the 43 drainage basins considered. Data for Chesapeake Bay are given in Table 12. The seasonality of pesticide use in each region is also given. For example, atrazine is applied in April-July in Maryland, April- May in Delaware, and March-May in Virginia.

For a study of pesticide drainage into Lake Erie, Baker and Richards (1990) compiled a list of the most used herbicides and insecticides in the Lake Erie basin (Table 13). Herbicides

TABLE 12. Pesticide Use in the Chesapeake Bay Drainage Basin (Metric Tons/Year).

<u>Herbicides</u>		<u>Insecticides</u>		<u>Fungicides</u>	
Alachlor	546	Carbofuran	128	Chlorthalonil	17.3
Atrazine	483	Chlorpyrifos	45.5	Metiram	3.47
Metolachlor	279	Ethoprop	38.1		
Cyanazine	141	Malathion	31.2		
Linuron	114	Carbaryl	29.7		
Simazine	98.3	Terbufos	19.9		
Butylate	60.0	Disolfoton	12.0		
2,4-D	42.6	Phorate	8.69		
Trifluralin	24.6	Permethrin	7.69		
Vernolate	24.1	Endosulfan	6.97		
Actifluorfen		Methyl Parathion	5.20		
Bensulide	9.1	Fenvalerate	2.36		
		Diazinon	1.75		
		Parathion	0.84		
		Methamidophos	0.64		

Source: Pait *et al.*, (1992, pp. 96-97).

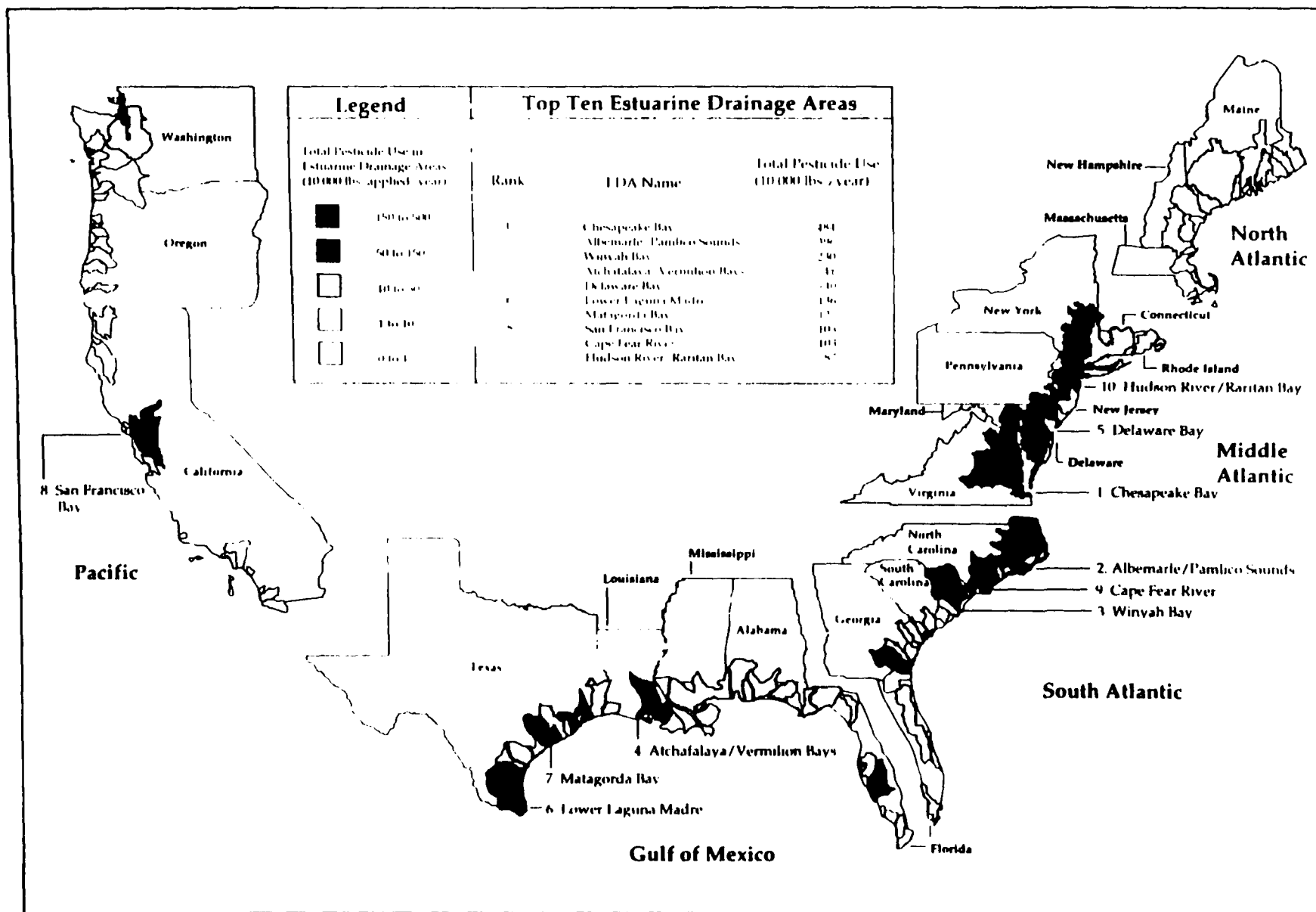


Figure 22. Agricultural pesticide use in estuarine drainage areas. Source: Pait *et al.* (1992).

Table 13. Pesticide Use in the Lake Erie Basin for 1986 and Ranking by Use in the State of Ohio for 1982.

<u>Pesticide</u>	<u>Brand</u>	<u>Type<sup>a</sup></u>	<u>Quantity Used (metric tons)</u>	<u>1986 Rank, by Use</u>	<u>1982 Rank by Ohio Use<sup>b</sup></u>
Alachlor	Lasso	H	1319	1	1
Metolachlor	Dual	H	897.2	2	3
Atrazine	Aatrex	H	783.9	3	2
Cyanazine	Bladex	H	273.4	4	4
Metribuzin	Lexone, Sencor	H	255.5	5	7
Chloramben	Amiben	H	155.5	6	6
Linuron	Lorox, Linurex	H	133.0	7	8
Terbufos	Counter	I	74.67	8	10
Trifluralin	Treflan	H	65.7	9	12
Butylate	Sutan, Genate plus	H	58.19	10	5
Dicamba	Banvel	H	54.39	11	19
Pendimethalin	Prowl	H	49.49	12	17
Bentazon	Basagran	H	49.36	13	15
Carbofuran	Furadan	I	48.23	14	11
2,4-D	2,4-D	H	44.44	15	14
Chlorpyrifos	Dursban	I	36.33	16	NR
EPTC	Eradicane, Eptam	H	34.67	17	13
Phorate	Thimet	I	31.51	18	NR
Fonofos	Dyfonate	I	25.10	19	9
Simazine	Princep	H	24.82	20	16
Total herbicide use in the Lake Erie Basin. The 15 herbicides listed above make up 97.3% of the total herbicide use in the Lake Erie Basin.			4315.5		
Total insecticide use in Lake Erie Basin. The 5 insecticides listed above make up 87.9% of the total insecticide use in the Lake Erie Basin.			245.6		

Source: Baker and Richards, 1990 (p. 246).

accounted for 92% of all pesticide tonnages. Corn and soybeans received 99.7% of herbicide and 90.1% of insecticide applications. In all, 4561 metric tons of pesticides were used in the basin in 1986.

Johnson *et al.* (1992) estimated usage of several insecticides, herbicides, fungicides, and nematocides in Ontario, Quebec, and the Atlantic Provinces for use in their Toxic Chemicals Emissions Inventory. According to the authors, actual sales figures for individual chemicals were very difficult to obtain because of regulations protecting confidentiality. In some cases estimates were made by speciating reported sales of a pesticide class. For example, "triazine herbicides" were broken down into separate quantities of atrazine, simazine, cyanazine, and metribuzine according to their reported usage on particular crops. Other inventorying methods are described in their report.

Pesticide emissions for ONT and ENA were made by Johnson *et al.* (1992), by considering: a) volatilization from soils, b) volatilization from vegetation, c) wind erosion of soil, and d) spray drift losses during application. Pesticide application rates in ONT were based on estimates of usage in Ontario, Quebec, and the Atlantic provinces. The tonnages of herbicides reported by Gianessi and Puffer (1990) for the U.S. were used to calculate ENA emissions.

The Jury model was used to predict soil volatilization. Climatological estimates of soil water flux were made by difference between monthly evaporation and precipitation. Monthly values were combined to provide seasonal averages for the model. A single set of soil properties "typical of agricultural cultivated soils" was used.

Volatilization from foliage was estimated by assuming that 70% of the pesticide impacting vegetation evaporates in a span of 5-10 days and the other 30% is washed off by rain and returns to the soil. These are based on a study of persistence of pesticides on vegetation by Willis and McDowell (1987). Because the smallest grid size considered was 5 km, spray drift was considered to deposit, then re-evaporate. Emissions were thus included in the volatilization algorithm.

Windblown dust is most significant during tilling and in the early growing season. Johnson *et al.* (1992) noted that emissions on dust will only be a problem for persistent pesticides, most of which have been discontinued. They also felt that there were insufficient data on levels of these chemicals in soils to make a meaningful estimate of windblown dust releases.

Atmospheric emissions of pesticides for ONT and ENA are shown in Table 14. Johnson *et al.* (1992) note that approximately 2,700 metric tons of pesticides per year were released in

ONT, a quantity far exceeding emissions of PAHs, PCDDFs, and PCBs. In ONT the highest ranking chemicals were the dichloropropenes/propanes --nematocides used on tobacco. Atrazine, alachlor, metolachlor, and 2,4-D were the four most heavily emitted herbicides. The former three are used on field crops and soybeans, whereas 2,4-D is mainly used on grains. The picture is different for ENA, where the top five herbicides (in rank) were: 2,4-D, alachlor, atrazine, metolachlor, and trifluralin. Because of the usage patterns and properties of the pesticides, this rank of emissions is slightly different from the list of tonnages used (Table 10). The asterisks shown in Table 14, ENA column, refer to compounds for which U.S. inventory data were not available. For these, only emissions from the Canadian portion of the grid (ONT, Quebec, Atlantic Provinces) were used.

Figures for lindane and chlordane apply only to estimated releases from agricultural applications and do not reflect their use for seed treatment (lindane) and as a termiticide (chlordane). In the U.S. chlordane has been banned from agricultural usage for many years, and its use in termite control was stopped in 1988 (EPA, 1987c, Federal Register, 1988). Before this, large tonnages of chlordane and heptachlor were applied as termiticides (Table 9). Endosulfan releases are only for ONT and eastern Canada, since Johnson *et al.* (1992) had no data from the U.S. However from the Pait *et al.* (1992) report, it is clear that very large quantities of this insecticide are used in estuarine drainage areas, including Chesapeake Bay (Table 12, Figure 23). Pait *et al.* noted that endosulfan runoff was one of the major causes of pesticide-related fish kills in estuaries. Because of the above difficulties, emissions of OC insecticides from ENA are probably grossly underestimated.

The spatial distribution of herbicide emissions in ENA shows highest releases in the "corn and grain belts": western Ohio, Indiana, Illinois, Kansas, Minnesota, eastern Dakotas and Nebraska (the survey did not include western portions of these states). Fluxes in these regions were typically 19 - 38 kg/km<sup>2</sup>-y, with pockets exceeding the upper value. Fluxes in the south, southeast, and mid-Atlantic states were 0.6 - 4.8 kg/km<sup>2</sup>-y. Occasional areas with fluxes in the 4.8 - 9.6 kg/km<sup>2</sup>-y were located. A "hot spot" with fluxes of 9.6 - 19 kg/km<sup>2</sup>-y was found near Chesapeake Bay. This is in accordance with the high reported usage of herbicides in this drainage basin (Table 12, Figure 22). Fluxes in the north Atlantic states ranged from <0.03 -0.6 kg/km<sup>2</sup>-y.

The pattern of insecticide emissions in ENA was different. Highest releases were estimated for the southeast and mid-Atlantic states, certain areas of the Midwest (Ohio, Michigan, eastern Illinois, western Pennsylvania, southern Ontario), and western New York. In these regions fluxes were 0.64 - 2.56 kg/km<sup>2</sup>-y, with a few areas >2.56 kg/km<sup>2</sup>-y (central Michigan, southeastern North Carolina). These correspond largely with fruit and vegetable growing areas. Fluxes

TABLE 14. Estimated Speciated Pesticide Emissions in Ontario and Eastern North America, Kg/Y.

	<u>Estimated Emissions (kg)*</u>	
	<u>Ontario</u>	<u>ENA</u>
<b>Herbicides</b>		
Alachlor	195,200	7,243,000
Atrazine	220,700	4,874,000
Butylate	8,950	13,200**
Cyanazine	60,000	1,534,000
2,4-D	184,800	10,691,000
Linuron	99,900	108,700**
Metolachlor	156,900	3,646,000
Metribuzine	51,500	58,900**
MCPA	52,400	568,200**
Trifluralin	9,520	2,058,000
Total	1,039,900	30,795,000
<b>Insecticides</b>		
Carbaryl	19,650	1,872,000
Carbofuran	7,410	982,700
Chlordane	354	853**
Diazinon	8,580	219,600
Endosulfan	7,300	11,300**
Lindane	2	2,570**
Methoxychlor	1,390	2,110**
Total	44,680	3,091,000
<b>Fungicides</b>		
Captan	78,030	132,300**
<b>Nematocides</b>		
Chloropicrin	58,400	59,800**
Dichloropropenes/propanes	1,296,300	1,330,100**
Methylisothiocyanate	185,800	185,800**
Total	1,540,500	1,575,700

\* Values after rounding

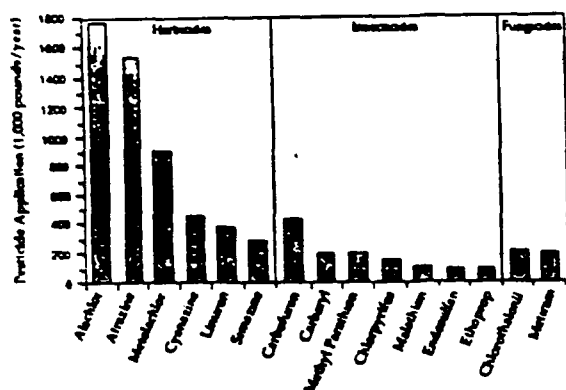
\*\* Data not available in the U.S.

Source: Johnson *et al.* (1992, p. 340).

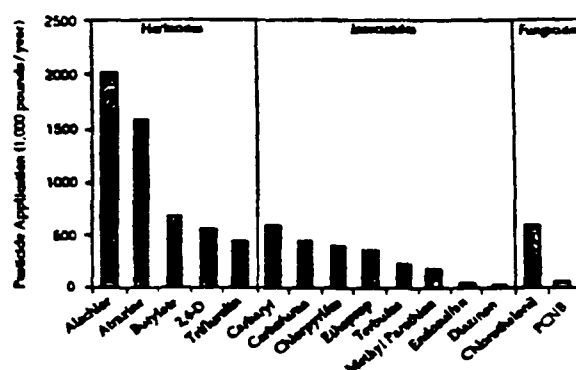


**Figure 23.** Application of selected pesticides (1000 pounds/y) in drainage basins of the middle Atlantic, south Atlantic, Gulf of Mexico, and Pacific regions. Source: Pait *et al.* (1992).

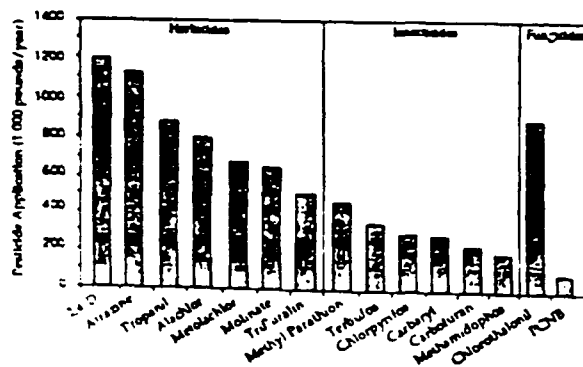
*Application of Selected Pesticides in the Middle Atlantic, 1987*



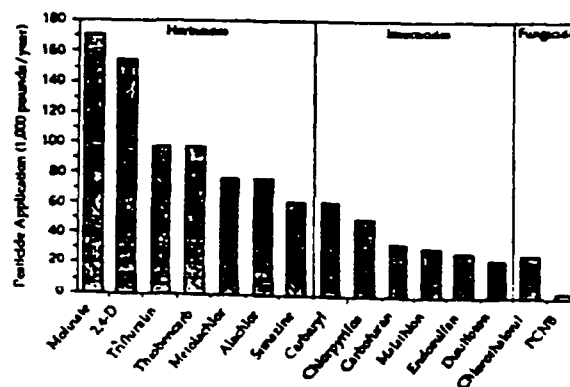
*Application of Selected Pesticides in the South Atlantic, 1987*



*Application of Selected Pesticides in the Gulf of Mexico, 1987*



*Application of Selected Pesticides in the Pacific, 1987*



throughout the "cotton belt", the Appalachians, and southern New England were lower: 0.04 - 0.64 kg/km<sup>2</sup>-y. Values for upper New England and the Atlantic Provinces were <0.01 - 0.08 kg/km<sup>2</sup>-y. Insecticide figures for ENA do not include fungicides and nematocides, and as noted above, releases of several other chemicals are for ONT and eastern Canada only. Emissions of insecticides are thus underestimated for many chemicals.

A separate inventory and atmospheric transport/deposition model was constructed for toxaphene by Voldner and Schroeder (1989). Toxaphene was very heavily used in the U.S., especially in the "cotton belt" during the late 1960s through mid-70s (Table 9). Usage declined thereafter, and production was banned in 1982. Remaining stocks were allowed to be applied until 1986. Voldner and Schroeder speciated total toxaphene use according to state and crop, using information from several reports referenced in their paper, surveys of U.S.D.A. Cooperative Extension programs at various universities, and an agricultural census of crop types.

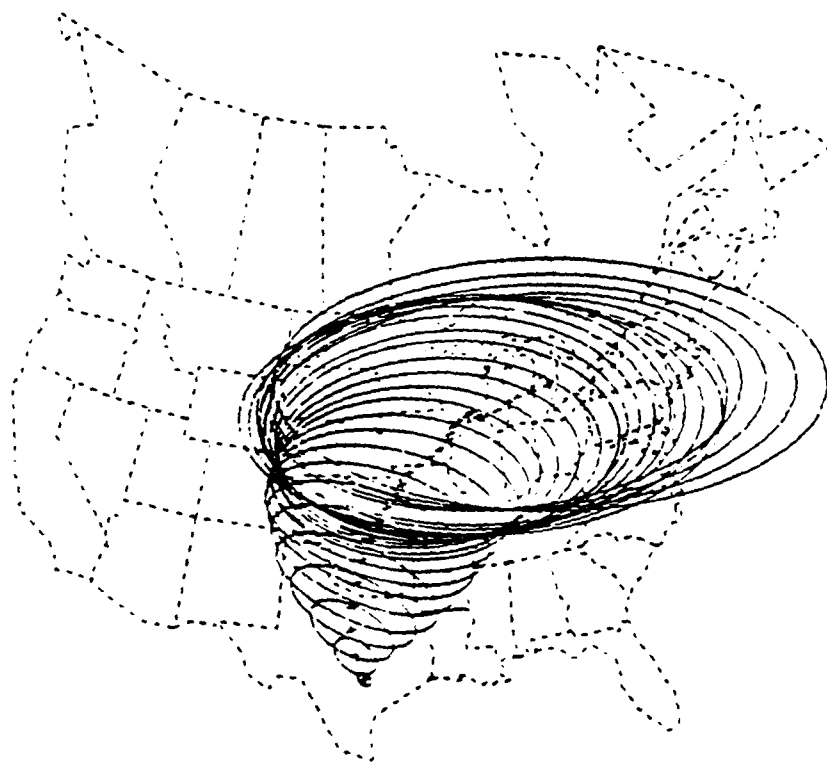
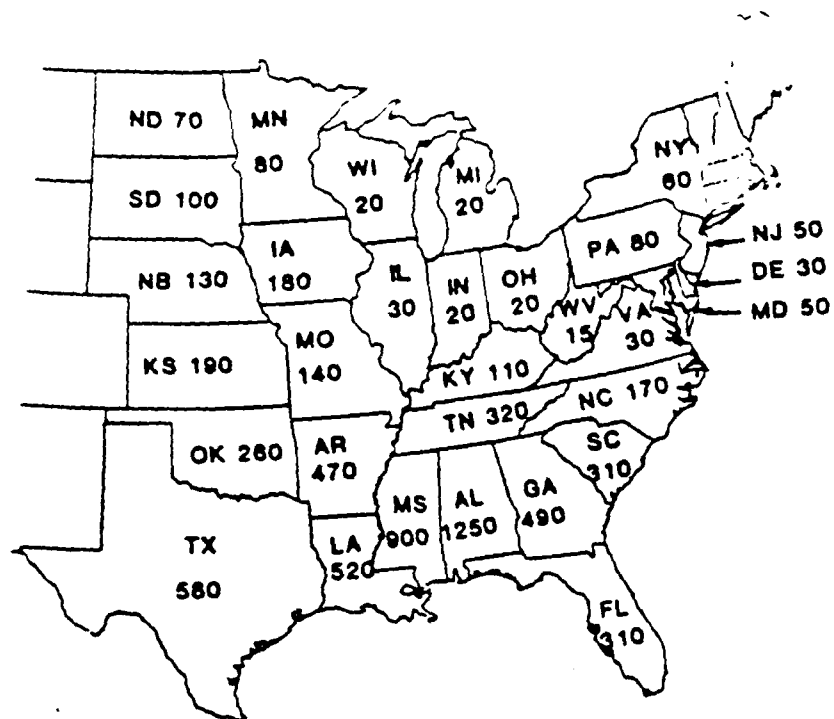
Apportioned toxaphene tonnages in eastern and midwestern North America for 1980 are shown in Figure 24.

## PCBs

Originally PCBs were used for a wide variety of purposes (Voldner and Smith, 1989). These were: closed system electrical and heat transfer fluids (approximately 60%), plasticizers (25%), hydraulic fluids and lubricants (10%), and miscellaneous uses (5%) which included flame retardants, additives to paints, inks, seal-ants, and carbonless copy paper. After 1971 uses were restricted almost entirely to closed electrical systems such as transformers and large capacitors.

According to Voldner and Smith (1989), 640,000 metric tons of PCBs were produced in the U.S., of which 70% were sold to manufacturers of transformers and capacitors. Approximately 40,000 metric tons were imported into Canada and another 3,000 metric tons entered Canada in manufactured fluorescent light ballasts and high intensity discharge lighting fixtures. As of 1982, the status of the 640,000 metric tons of PCBs in the U.S. was estimated to be:

• Destroyed	3%
• Exported	11%
• Buried in landfills	21%
• Still in service	54%
• Circulating in the environment	11%



**Figure 24.** Top: Estimated usage of toxaphene by state in 1980, metric tons/y. Bottom: Summer mean trajectory and spread of toxaphene emissions from Texas. Source: Voldner and Schroeder (1989).

PCBs are released into the atmosphere from both point and area sources. The former include municipal and hazardous waste land-fills, which contribute PCBs through volatilization and release with landfill gases (Murphy *et al.*, 1985; Lewis *et al.*, 1985). PCBs are also emitted by refuse and sewage sludge incinerators (Murphy *et al.*, 1985). Occasional leakage of transformers and capacitors, and emissions from other in-service equipment (e.g. old fluorescent light ballasts) releases PCBs on an area scale.

Like OC pesticides, PCBs are continually cycling through the environment and air-surface exchange is important in controlling their atmospheric concentrations. Several studies have shown that PCB levels in ambient air are temperature-dependent, much like the pesticides in Figure 16 (Hermanson and Hites, 1989; Hoff *et al.*, 1991b; Manchester-Neesvig and Andren, 1989; Larsson and Okla, 1989). Revolatilization of PCBs from surface water must be considered in the PCB balance of the Great Lakes (Achman and Eisenreich, 1992; Baker and Eisenreich, 1990; Hornbuckle *et al.*, 1992; Strachan and Eisenreich, 1988).

Because of the sporadic nature of PCB emissions, it is extremely difficult to predict quantities released to the atmosphere. Murphy *et al.* (1985) estimated that between 10 and 100 kg/y were emitted from sanitary landfills in the U.S., based on a survey of six sites in the Great Lakes area. At these landfills 70-500 ng of PCBs were expelled per m<sup>3</sup> methane. Differences among hazardous waste disposal facilities are very large. Lewis *et al.* (1985) found that PCB concentrations over "hot spot" chemical waste landfills greatly exceeded background concentrations, whereas emissions from a well-controlled facility were negligible. Based on other reports, Voldner and Smith (1989) estimated that PCBs released to the environment through accidental spills and municipal waste incineration were 50,000 and 5000 kg/y, respectively.

Johnson *et al.* (1992) identified the most important sources of PCBs to the atmosphere as:

1. Transformer leakage
2. Electric power generation
3. Industrial fuel combustion
4. Landfills
5. Sewage sludge combustion
6. Waste oil combustion

Transformer leakage/spillage estimates were based on a report for utility industry closed-system equipment in the U.S. These losses as percentages of total PCBs contained in the equipment were: large transformers (0.027%), large capacitors (0.42%). A loss rate of 0.24% for

the industry was assumed. Of the spilled PCBs, 0.3% was estimated to be evaporated before cleanup. The overall atmospheric emission factor was 7.2 mg for each kg PCBs contained in transformers and capacitors ( $0.0024 \times 0.003 = 7.2 \times 10^{-6} = 0.00072\%$ ).

The information for (2) and (3) was based on very limited data on PCB emission factors from bituminous coal combustion. These were 0.65 mg/metric ton coal for utility boilers and 3-26 mg/metric ton for industrial coal-fired stokers. It is not known why coal combustion should be a source of PCBs. Emission factors (mg/metric ton) for incineration sources were given by Johnson *et al.* as follows: industrial liquid waste 1.18, commercial waste: 2.5, hospital: 29, waste oil 390, sewage sludge (0.69-14, 5.4 selected), municipal solid waste 1.3-4.5.

The PCB release estimates of Johnson *et al.* from open sources (including transformer and capacitor leakage and landfills), incineration, and stationary fuel combustion are summarized in Table 15. Only 38 kg/y was attributed to solid waste incineration in ENA. This differs markedly from a U.S. municipal waste combustion study (quoted by Voldner and Smith, 1989) which estimated about 5000 kg/y from this source. The atmospheric release of PCBs to ENA from transformer and capacitor leakage was 370 kg/y. Voldner and Smith quote a report which estimated that 50,000 kg/y PCBs were spilled in the Great Lakes region. Applying the evaporation factor of Johnson *et al.* (0.3%) yields 150 kg/y PCBs entering the atmosphere.

No inventory has considered re-emission of PCBs from soil, plants, and water; and this may be a significant part of the mass balance. Also, as Voldner and Smith point out, the availability and data quality for PCB emissions "leaves a lot to be desired"

When displayed on a gridded scale (Johnson *et al.*, 1992), highest emissions of PCBs occurred in a broad belt extending from Illinois eastward to the mid-Atlantic and southern New England states. In this region fluxes were generally 0.32 - 3.2 g/km<sup>2</sup>-y (= µg/m<sup>2</sup>-y). This is remarkably similar to the 1.5-1.8 µg/m<sup>2</sup>-y precipitation and dry deposition fluxes out of the atmosphere estimated for the Great Lakes (Eisenreich and Strachan, 1992).

Other areas with atmospheric emissions of the same magnitude were Chicago - Milwaukee, southeastern Michigan, a band around southern and western Lake Ontario, and some populated areas in the south. A few pockets with fluxes of 3.2 to >32 g/km<sup>2</sup>-y were identified. Elsewhere fluxes were usually in the 0.032 - 0.32 g/km<sup>2</sup>-y range. Fluxes north of the Great Lakes and in eastern Canada were <0.001 -0.032 g/km<sup>2</sup>-y.

#### 4.2. Emission profiles for major source categories

Emission source profiles provide a useful tool for quantifying the contributions of pollutants from various sources in a given region. This is particularly true in the cases when actual emission measurements are not available. Chemical mass balance (CMB) analysis is then frequently used which requires information about source profiles. It is desirable to prepare a set of emission source profiles for fine and coarse particles separately. The CMB receptor modeling has been described in the literature (Miller *et al.*, 1972; Gordon, 1980, 1988; Winchester and Nifong, 1971; Watson *et al.*, 1984).

An important step of the CMB analysis is construction of emission source profiles. A detailed description of emission sources and emission generating processes is needed first. This information has been created for the Great Lakes region as mentioned above. Then the emission source profiles have been constructed using information on emission factors for several trace elements and persistent organic compounds, such as PAH, polychlorinated di-benzo dioxins (PCDD), polychlorinated di-benzo furans (PCDF), and PCBs. The profiles were constructed on the basis of emission factors calculated for the global emission survey for trace elements by Nriagu and Pacyna (1988) and emission factors from the Ministry of the Environment (MOE) Toxic Chemical Emission Inventory for Ontario and Eastern North America by Johnson *et al.* (1992).

The emission source profiles for the combustion of coal in utility, industrial, and residential boilers, the combustion of residual oil in utility and industrial boilers, the production of copper, lead, and zinc in primary and secondary plants, the production of iron and steel, the incineration of municipal wastes and sewage sludge, the production of cement as well as phosphate fertilizers, the combustion of wood in stoves, and fireplaces, and the combustion of gasoline and diesel oil in mobile transportation are presented in Figures 25a-c.

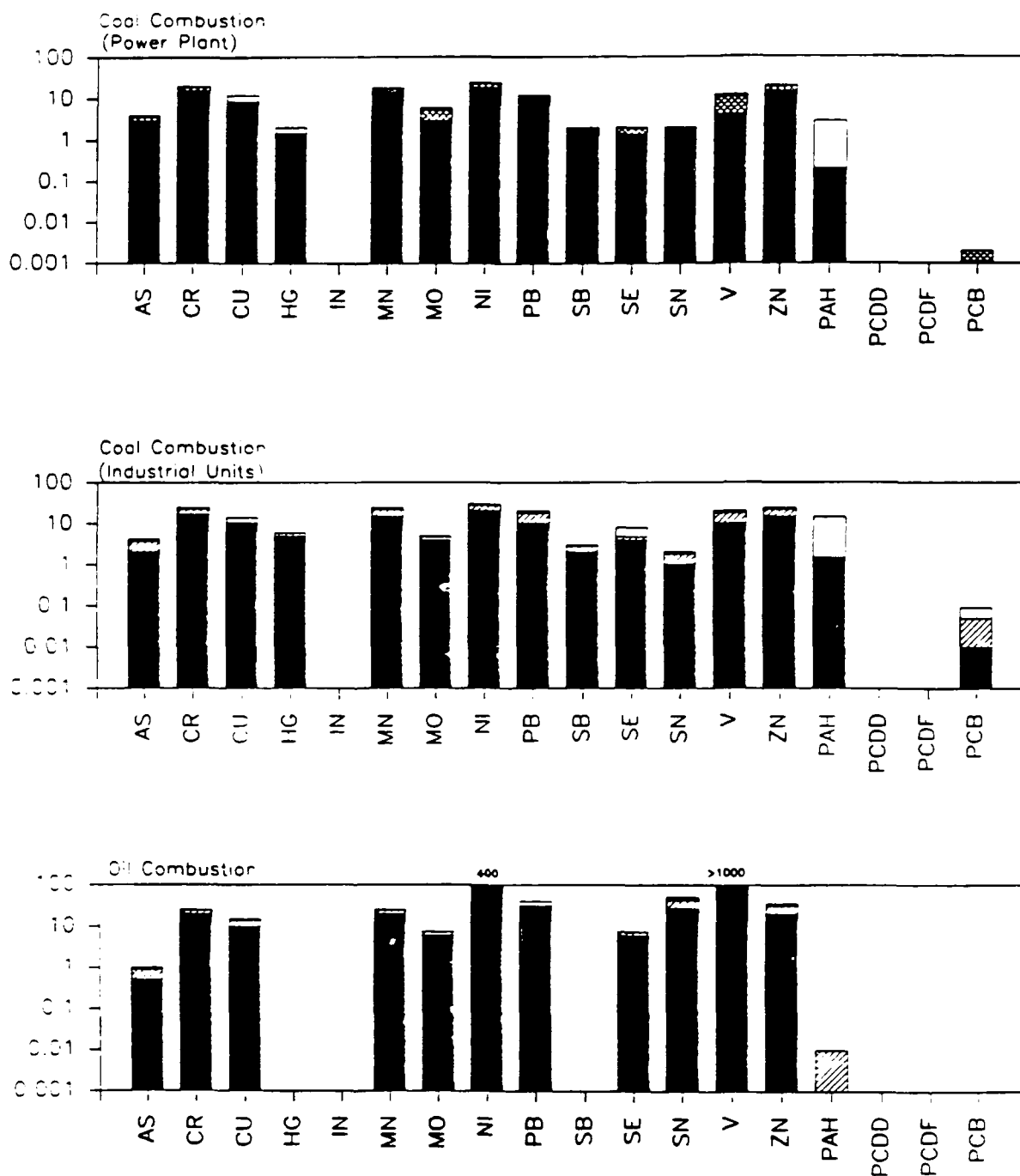
The emission source profiles as shown in Figures 25a-c can then be used to construct regional emission profiles for the Great Waters area by combining information on the source profiles with information on contribution of a given emission source category to a total emission of a studied compound in the region. Regional emission profiles are used to assess emission contribution from various regions to the air concentration or deposition at a given receptor.

TABLE 15. Atmospheric Emission of PCBs in Ontario and Eastern North America, kg/y.

	<u>Ontario</u>	<u>Eastern North America</u>
Open sources <sup>a</sup>	36.9	453.2
Waste incineration	1.3	38.2
Stationary source combustion	12.2	434.9

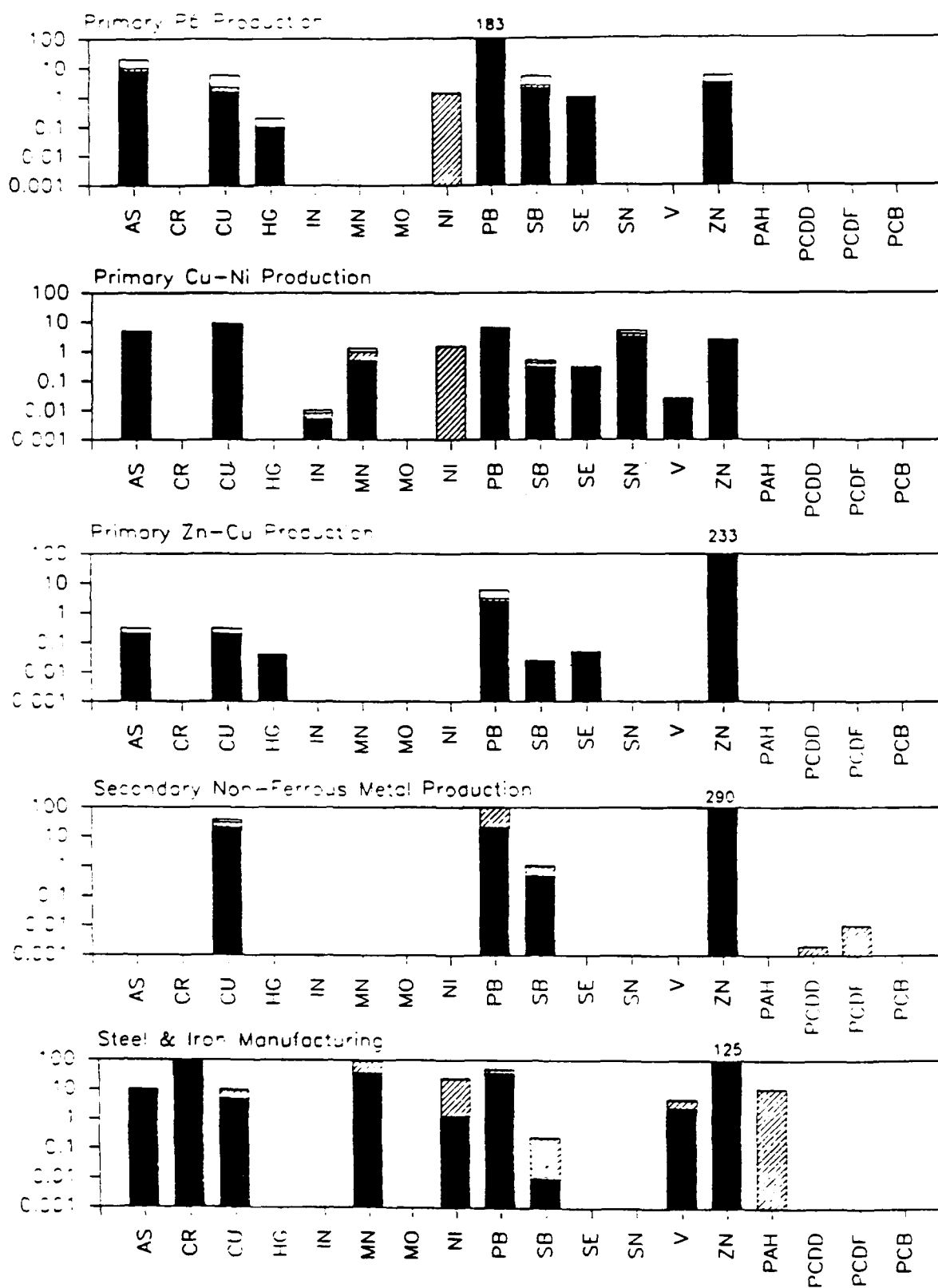
a) Includes transformer & capacitor leakage (80%) and emissions from landfills (20%).

Source: Johnson et al. (1992, pp. 263, 266, 333).



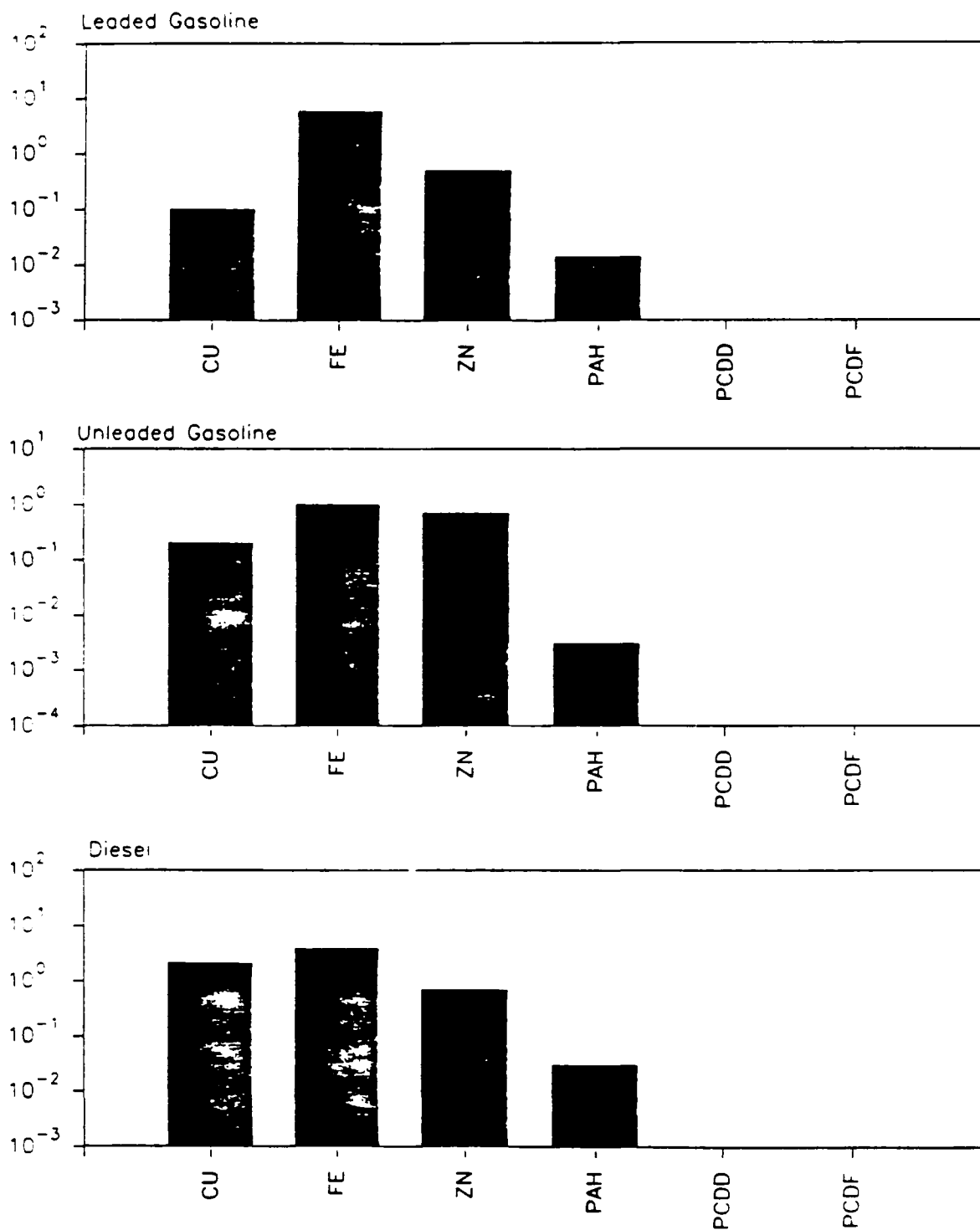
**Figure 25a.** Emission source profiles for major source categories estimated with cadmium as a reference element.





**Figure 25b.** Emission source profiles for major source categories estimated with cadmium as a reference element.

## Mobile Transportation



**Figure 25c.** Emission source profiles for major source categories estimated with cadmium as a reference element.

#### 4.3. Emission profiles for diffuse sources of organics

The earth's surface is a vast reservoir for pesticides and other organic chemicals. Exchange of gaseous SOC's is a two-way process; and plants, soils, lakes, and oceans act as both sources and sinks of airborne chemicals. Examples are volatilization of pesticides from sprayed foliage vs. uptake of pesticides from the air by pine needles. Since these exchanges occur, transport of pesticides is not a simple source-to-sink relationship. Deposition and re-evaporation of the chemical may occur many times during transit, in what is becoming known as the "grasshopper effect"

Understanding the processes underlying these cycles is critical to developing transport and deposition models for pesticides and determining sources to the Great Waters. Below three processes are discussed, volatilization from soils, gas exchange with water, and gas exchange with plants. The two-way nature is emphasized for the latter two. In the case of soil, uptake of gaseous pesticides in non-target areas is poorly understood. The intent is to present an overview of the processes and their significance. Mathematical details are given in the references.

##### 4.3.2 Air-surface exchange processes

###### a) Volatilization from Soils

Although spray drift can have a local impact, post-application volatilization is a more important pathway of pesticide loss from fields. Many early studies are referenced in work by Nash and Hill (1990) and Spencer and Cliath (1990). These investigations have been done by following pesticide disappearance from soils under field conditions, and also through controlled experiments in agroecosystem chambers. Major losses can take place within a few days if the chemical is applied to soil surfaces. Incorporation into the soil layer greatly reduces volatilization; but even so, long-lived pesticides continue to evaporate. Spencer and Cliath (1990) state that: "Even in areas where DDT use has been discontinued, the persistence of DDT residues is sufficiently great that they will continue to be redistributed for many years. In these areas, volatilization from the soil probably will be the main source of DDT components moving into the atmosphere ..."

If not washed off by rain or irrigation, pesticides are quickly evaporated from foliage. In the absence of precipitation, Willis *et al.* (1985) found half-lives for toxaphene, methyl parathion, and fenvalerate on cotton plants of 0.7, 0.1, and 3.3 days. In another study (Seiber *et al.*, 1979),

toxaphene which was aerially sprayed on a cotton field disappeared rapidly from the foliage, with 59% lost in 28 days. Loss of toxaphene in the aerated top soil was slower, 51% in 58 days.

The fate of diazinon sprayed on a dormant peach orchard was followed by accounting for the amount of pesticide in air, soil, and tree parts (Glottfelty *et al.*, 1990). Spray drift and volatilization during application were small, and were exceeded by evaporation losses over the next two days. After the first 24 h, diazinon in the soil dissipated by a first-order process with a 19-d half life. The conclusion was that most of the diazinon in the atmosphere of California's Central Valley comes from volatilization.

A mass balance for a DCPA-treated onion field yielded a half-life of 40.5 days for the herbicide. Flux measurements based on air samples taken above the plot showed that in that time 29% of the DCPA was lost by volatilization (Ross *et al.*, 1990).

In the tropics OC pesticides are heavily used and volatilization is the main loss process. A mass balance of HCH in the Vellar River estuary (India) showed that of 42,000 kg HCH applied, 41,830 kg (99.5%) evaporated and only 170 kg was transported by the river (Takeoka *et al.*, 1991). Yeadon and Perfect (1981) found that DDT applied to soils in Nigeria evaporated with a half-life of 9 days.

Field measurements of pesticide volatilization are time-consuming and costly. A classic paper by Parmele *et al.* (1972) described several micrometeorological techniques and used them to determine losses of heptachlor and dieldrin from bare soil and corn fields. Common methods are briefly described below. For details, see papers by Parmele *et al.* (1972) and Majewski *et al.* (1989, 1990). All of these flux methods except the last (TPS) require measurement of the vertical gradient in pesticide concentration.

Typically this is accomplished by collecting air samples at five or more heights above the soil up to a few meters.

- Thornthwaite-Holzman, or Aerodynamic (AD): This is the most frequently used field technique, and is based on accurate measurements of pesticide and wind speed gradients in the turbulent boundary layer. Requirements are a large, uniformly surfaced area with similar land surrounding it, and a long fetch (unobstructed upwind distance).
- Lysimeter and Energy Balance (EB): These methods describe pesticide fluxes (F, mass/area-time) by the general equation:

$$F = K_z(dC/dz) \quad (3)$$

where  $K_z$  is the vertical diffusivity and  $dC/dz$  is the pesticide concentration gradient above the surface. Flux estimation methods assume that  $K_z$  of pesticide vapor and water vapor or heat are the same.  $K_z$  is determined by direct measurement of water loss from a weighing Lysimeter, or (more commonly) by energy balance. In the latter technique, vertical gradients of temperature and humidity above the surface are used with measured radiation and soil heat fluxes to deduce  $K_z$ . Field size requirements are the same as those for the AD method.

The method is simple, but the EB instrumentation is sophisticated.

- **Integrated Horizontal Flux (IHF):** Fluxes from the field can be calculated from the vertically integrated pesticide concentration and wind profiles. This was used by Glotfelty *et al.* (1990) to determine transport of volatilized diazinon from a treated orchard:

$$F = (1 / R) \int C \cdot u \cdot dz \quad (4)$$

In Equation (4),  $C$  and  $u$  are average pesticide concentrations and wind speeds at a particular height,  $z$ .  $R$  is the distance the wind has to travel over the treated surface. In practice, the integral is estimated by summing over finite height intervals. The method requires a uniform surface and a uniform source strength, but is independent of assumptions regarding the equivalence of pesticide, water vapor, and heat  $K_z$  values. Also, fetch requirements are not as critical. However, IHF gives no information above the highest and lowest sampling point.

- **Eddy Correlation (EC):** In the EC method pesticide fluxes are determined by measuring short-term fluctuations in vertical heat flux. The technique requires meteorological equipment that can respond rapidly to small changes in temperature, wind speed, and wind direction. As in the EB method, it is assumed that  $K_z$  are the same for heat and pesticide vapor. Disadvantages are complexity of instrumentation, need for fast-response sensors, and precise alignment requirements.
- **Theoretical Profile Shape (TPS):** A trajectory simulation model predicts that there is a point above the center of a circular-shaped source where the gaseous horizontal flux to the atmosphere can be determined from measurements of wind speed and mean pesticide air concentration at that point. In contrast to the above methods, TPS requires measurement of wind speed and pesticide concentration at only one height. A drawback is that field plots must be circular.

AD, IHF, EB, EC, and TPS methods were compared in a field test of volatilization from fallow soil of four pesticides: lindane, diazinon, nitrapyrin, and chlorpyrifos (Majewski *et al.*, 1990). No statistical differences were found at the 95% confidence level for all methods and compounds. However the authors cautioned that it is not clear whether any of the methods are accurate -- that is, if they describe what is really occurring. Careful mass balance experiments were suggested as a way to calibrate flux estimation methods.

The expense and time required to do these studies have greatly limited the number of field experiments that have been carried out over the years. Moreover, results are likely to be highly dependent on local soil properties, meteorological conditions, and pesticide application methods.

Concurrent with the development of methods for flux estimation have been experiments to identify the factors that influence pesticide volatilization. Much work has been done in field plots and environmental chambers and to follow pesticide dissipation from soils. Recent studies and previous work are described by Nash and Hill, 1990; Spencer and Cliath, 1990; Clendening *et al.*, 1990; Jenkins *et al.*, 1990; and Woodrow *et al.*, 1990.

In a series of four papers, Jury *et al.* (1983, 1984a-c) described the development and application of a model for assessing the behavior of organic compounds in soil. Losses of chemicals from soil are the result of leaching, volatilization, and degradation. The Jury model incorporates all three processes. To apply the model, it is necessary to know:

- Properties of the chemical. Henry's law constant (H), soil organic carbon - water partition coefficient ( $K_{OC}$ ),

Diffusion coefficients in water and air, reaction rate coefficients (parameters of first-order loss equations that describe chemical and microbial reactivity). The latter are difficult to assess.

- Soil properties. porosity, bulk density, volumetric water content.

In addition, fluxes are affected by the amount of chemical applied, depth of incorporation into soil, temperature, and relative humidity.

The Jury model views pesticide evaporation as being controlled by two resistances, the soil layer and the air boundary layer.

That is, emissions of gaseous pesticides are related to: a) the supply of pesticides from below to the soil surface, and b) the volatilization rate from the soil surface into the atmosphere.

The former process occurs by vapor-phase diffusion in soil pores and movement of dissolved chemical upward with water flow.

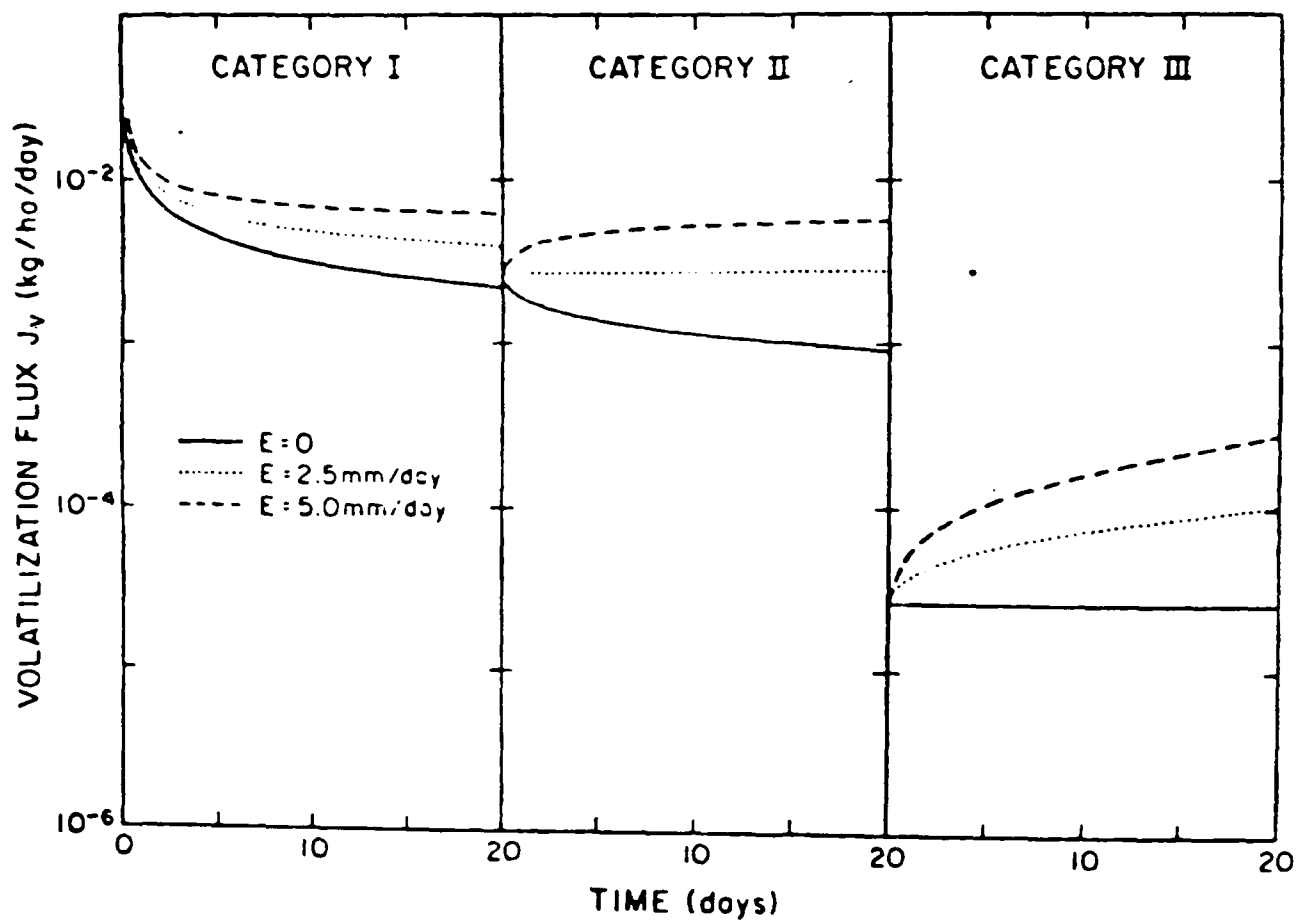
For some chemicals water evaporation from the soil is critical, because it causes an upward flow of water which transports chemical to the surface. If water flow carries an insignificant amount of chemical relative to vapor diffusion, water evaporation has less effect. Jury *et al.* (1984a) and Spencer and Cliath (1990) show how, based on their physicochemical properties, substances can be classified by the effect of water evaporation on their volatility from soils (Figure 26):

- Class I. High Henry's law constants (OCs, EPTC, triallate, trifluralin). These chemicals volatilize from the surface faster than mass transport can replenish them from below. Control thus resides in the soil. Volatilization rates are increased by evaporation of water for some of these compounds, but not others. The influence of water flux is less than for Class II and III compounds. Volatilization rates decrease with time.
- Class III. Low Henry's law constants (atrazine, prometryn, napropamide, 2,4-D). These move to the surface in water flow faster than they can be lost to the atmosphere through the boundary layer. Without water evaporation their volatilization rates are very low. As water evaporates, pesticide concentrations build up at the soil surface and volatilization rates increase with time.
- Class II: Intermediate in behavior (methyl parathion, parathion, ethoprophos)

From Figure 26 and the further description of chemical classifications (Jury *et al.*, 1984a), it is fair to say that for most pesticides water evaporation will play an important role in loss from soils.

In the final paper of the series (Jury *et al.*, 1984c) the authors compare results of the behavior assessment model to volatilization data from laboratory chamber experiments. Very good agreement was obtained, and the effects of water evaporation for chemicals in the different volatility classes were correctly predicted. Despite this, Jury *et al.* (1984b) stressed that the model is to screen chemicals for their behavior in soils, not to simulate field results. In field mass balance studies (Clendening *et al.*, 1990) volatilization behavior of five Class I and III compounds was in accordance with the Jury model, however deep migration by leaching was difficult to predict.

Several field models have been developed to simulate pesticide volatilization. A six-compartment model was formulated by Nash and Hill (1990) to take into account changing



**Figure 26.** Volatilization flux rates for a prototype chemical from each category of volatilization behavior as affected by water evaporation ( $E$ ). Source : Jury *et al.* (1984b); Spencer and Clith (1990).



mechanisms of loss over time. When first applied to a soil surface, pesticides volatilize quickly. Later the loss rate slows down, in part due to adsorption of chemical to the soils.

Woodrow *et al.* (1990) investigated volatilization of three herbicides and methyl parathion from flooded rice fields in California's Sacramento Valley. Good agreement was found between measured loss rates and those predicted by EPA's EXAMS model. A Gaussian plume dispersion model (ALOHA) was used to estimate transport of the chemicals out of target areas. Measurable air concentrations of pesticides in residential and business areas were due to drift during application, post-application volatilization, and photooxidation of pesticides during transport (conversion of methyl parathion to its oxon).

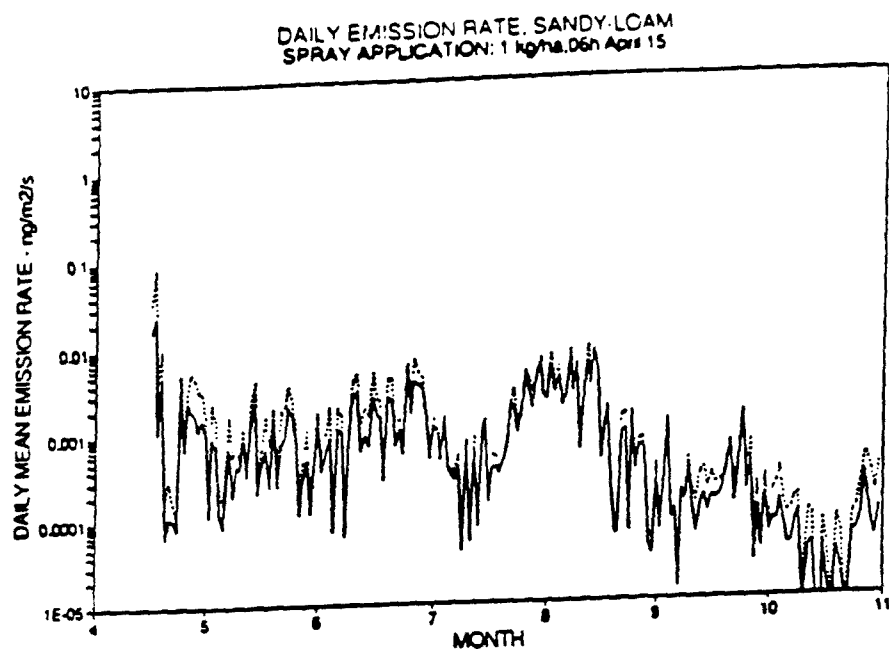
A volatility model that takes into account changing meteorological conditions, soil temperature and moisture, and water evaporation rates over the period of interest was developed by Scholtz and Voldner (1992), who then applied it to the evaporation of three pesticides (lindane, chlordane, and 2,4-D) from sandy loam soil. Modeled daily emission rates and the cumulative fraction of pesticide lost over a 6.5-month period are shown in Figure 27. Although the Henry's law constant of the pesticides change with temperature, including this temperature dependence had little effect on the results. Differences in water evaporation rates had the strongest influence on daily fluxes.

#### b) Air-Water Gas Exchange

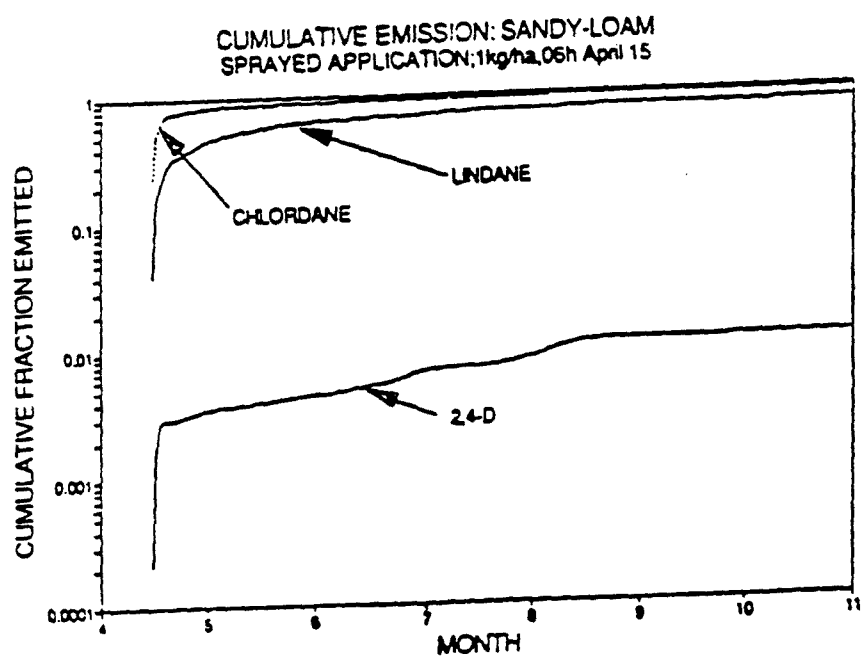
In the frequently used "two-film" model gases are exchanged by diffusion through thin air and water films on either side of the air-water interface. The rate at which molecules diffuse through these films is slow compared to convective mixing in the bulk air and water, and thus the interface acts as a resistance to transfer. The equations for describing flux ( $F$  = mass/area-time) of material have the form:

$$F = K\Delta C \quad (5)$$

where  $\Delta C$  is the concentration gradient (that is, difference in concentration from the top to the bottom of the air or water film). The overall mass transfer coefficient ( $K$ ) takes into account the resistance of both films. Algebraic expressions for  $K$  include transfer constants for the individual air and water phases and the Henry's law constant of the chemical. Often the resistance of either the air or water will dominate, and the chemical is said to be "gas phase" or "liquid-phase" controlled. Which situation applies is largely related to the Henry's law constant.



Modelled mean daily emission rate of 2,4-D: Henry's Law coefficient a function of temperature (solid); independent of temperature (dotted).



**Figure 27.** Modeled daily emission rates and cumulative fractions emitted for pesticides sprayed on sandy loam soil. Top: lindane; Bottom: lindane, chlordane, and 2, 4-D. Source: Scholtz and Voldner (1992).

The detailed equations for two-film gas exchange of pesticides, PCBs, and PAHs have been presented by many authors, including Baker and Eisenreich (1990), Corns and Bidleman (1991), WMO (1989), Hinckley *et al.* (1991), and McConnell *et al.* (1992).

As a way of quantitatively describing water bodies as sources or sinks, the model has many shortcomings. Major unknowns are:

- Mass transfer coefficients as a function of wind speed.
- The role of bubbles and breaking waves in the exchange.
- Henry's law constants of SOC's as functions of temperature and salinity.
- Physical states of SOC's in air and water: To employ the model, it is necessary to know the fraction of gaseous and dissolved compound. Further method development is needed to speciate SOC's in air and water into gaseous, particulate, colloidal, and dissolved components.

Calculations based on the two-film model indicate that gas exchange of SOC's is an extremely important factor in the Great Lakes budget. Murphy (1983) proposed evasion of PCBs from the Great Lakes, and a subsequent mass balance study concluded that the net flux of PCBs and DDT was out of the lake on an annual basis (Strachan and Eisenreich, 1988). At that time these conclusions were based on limited air and water data. Mass balance models of Siskewit Lake also show the importance of volatilization (McVeety and Hites, 1988; Swackhamer *et al.*, 1988; Swackhamer and Hites, 1988).

Recent paired air and water measurements have provided much more insight to this process. Data from Lake Superior indicated volatilization of PCBs during late summer (Baker and Eisenreich, 1990). Intensive studies in Green Bay showed that PCBs volatilized from the surface water at rates ranging from 13 - 1300 ng/m<sup>2</sup>-d. Moreover, the profile of individual PCB congeners was different in the air over Green Bay than over land (Achman *et al.*, 1992; Hornbuckle *et al.*, 1992).

Concurrent sampling of air and water in Green Bay and the lower four Great Lakes allowed McConnell *et al.* (1992) to determine the direction of HCH exchange. Transfer of HCHs to Green Bay was air-to-water (deposition) in early June. In August when surface waters were warmer, the flux direction was reversed (volatilization) in Michigan, Huron, and Erie, but remained depositional in Ontario. Based on the annual cycle of HCHs in the atmosphere (Hoff *et al.*, 1991a), the authors predicted that transfer of gaseous HCHs was into the lakes for most of the year, with short periods of volatilization in late summer. The loading of HCHs to lakes Michigan, Huron, Erie, and Ontario by gas deposition was estimated to be 370 kg/y. By

comparison, 970 kg/y entered the four lakes by precipitation and dry particle deposition (Eisenreich and Strachan, 1992).

Gas exchange contributes significant quantities of OCs to the oceans. The GESAMP report (WMO, 1989) concluded that air-to-water gas transfer of OCs accounted for 24-72% of total atmospheric deposition. Cotham and Bidleman (1991) estimated that about 110 metric tons/y of HCHs entered the Arctic, about two-thirds of which came from gas uptake by the surface ocean. Gas exchange formed 20-60% of the total atmospheric budget for other OC pesticides.

### c) Air - Plant Exchange

Plants accumulate OCs from the atmosphere, and many investigators have suggested their use to survey atmospheric contamination in non-agricultural and remote regions. The case of pine needles as an indicator of DDT transport from eastern Europe was mentioned earlier (Section V-C-1c). Examination of different plant species from around the world revealed especially high levels of DDT, HCHs, and PCBs in China. DDT was also high in plants from several African countries, and in Russia near Moscow. Lowest concentrations of most pesticides and PCBs were found in lichens from the Antarctic Peninsula (Bacci *et al.*, 1986, 1988; Gaggi *et al.*, 1985; Villeneuve *et al.*, 1988).

Accumulation of pesticides and PCBs by plants is important for several reasons. The potential for using plants as a monitoring tool was mentioned above. Plants are also at the base of the terrestrial food chain. Transfer of OCs from lichen to reindeer to man was investigated in northern Sweden (Villeneuve *et al.*, 1985). The percentage of transfer from lichen to reindeer was positively correlated with the octanol-water partition coefficient ( $K_{ow}$ ) of the compound.

Finally, the earth's plant biomass is a large reservoir for persistent organic compounds. Accumulation from the atmosphere into plants is related to the proximity of sources (i.e., concentration of chemical in air) and temperature. The strong role of temperature was shown by Calamari *et al.* (1991), who surveyed plants from around the world for OC pesticides and PCBs. HCB concentrations in plant tissue were highest in the Arctic and Antarctic and lowest in equatorial regions. For this compound the "source factor" can be eliminated, because concentrations of HCB in the troposphere are uniform, varying by no more than a factor of 2-3. Levels of HCHs and DDT were far higher in temperate and tropical zones than at the poles, showing the strong dependence on regional use of these pesticides.

Recent work has focused on the rate and mechanism of atmospheric uptake and depuration of OCs by plants. Like fish in water, plants take up chemical from a polluted atmosphere and release it when placed in clean air (Bacci *et al.*, 1990a,b). The steady-state bioconcentration factor ( $BCF = \text{concentration of chemical in the plant divided by that in air}$ ) is related to two common physicochemical properties,  $K_{ow}$  and  $H$ :

$$BCF = \text{constant} \cdot K_{ow}RT/H \quad (6)$$

Reviews of accumulation processes and comparison of different models have been written by Paterson *et al.* (1990) and Schonherr and Reiderer (1989).

The idea that large areas of "green space" on the planet can take up and release pesticides to the atmosphere has important consequences for long-range transport and seasonal cycles of pesticides in the atmosphere.

#### **4.4. Evaluation of emission inventories. Comparison with European studies**

In general, emission inventories have only recently been compiled for toxic heavy metals and persistent organic compounds, with the exception of lead. Emission inventories were first used to evaluate the environmental impacts of the emissions from single point sources, thus were of local importance. In the late 1970's, it was recognized that heavy metals can be transported for distances of up to a few thousand kilometers. This suggested the need for regional, and even global, emission inventories to be formulated for these persistent pollutants. When the parameters affecting the emission quantities were defined for this study, it became clear that a regional emission inventory for heavy metals should be prepared using so-called bottom-up approach. In other words, major emission sources should be identified and emission quantities assessed in sub-regions, e.g. administrative units such as county or city, and then added in order to obtain emissions within a region. In this way a detailed assessment of emission sources can be collected at a county or city level.

Emission measurements are often carried out at specific sources and their results are then reported at a sub-region level. Indeed, measured data have been used to assess emissions of toxic pollutants in various states in the study region. This applies particularly to emissions from single point sources, and mainly waste incinerators. The emission data obtained through such approaches are usually accurate providing that the measurements are representative with respect to sample collection and analytical methods used. Thus, the above approach is recommended for collection of emission data from major point sources, including large power plants (e.g. over 1000

MW electricity), heat boilers (e.g. 200 GJ/h capacity), primary and secondary non-ferrous metal smelters, cement kilns and already mentioned waste incinerators. In Europe, there are already regulations requiring emission data to be measured for large power plants within the parties of the Commission of the European Communities. Standardization of measurement methods and harmonization of reporting procedures are important factors when the bottom-up approach is used to obtain emission data. These factors need to be employed in order to assure the comparability of the emission data to be used to construct the emission inventory for a given region.

There are currently very few measurements on the emissions of hazardous air pollutants from sources within the Great Waters regions. One reason for this could be that on the national scale in the U.S. there is no formal obligation to undertake an emission survey for toxics, the TRI program being voluntary. Only some states have taken the initiative to prepare emission surveys, mostly using emission factors from the literature and statistical information on the production of industrial goods and the consumption of raw materials. The measured data reported for the study region are more accurate than the estimated values. The measured source profiles provide information which may be used when estimating emissions for regions with no measurements.

The second approach used to prepare an emission inventory is called a top-down approach and is used when the inventory is based on emission estimates. The emission inventories prepared by EPA, IJC, and the Canadian authorities, and used in this report, are based on the top-down approach. Major emission source categories for a larger region, e.g. a state are defined in the first step, emission factors are selected, and emission quantities calculated. Further division of these estimates in order to obtain spatial distribution of emissions is carried out using either surrogate parameters, such as population density maps for distribution of area source emissions or a list of point sources with information on geographical location and emission data for other compounds, such as sulfur and nitrogen oxides, volatile organic compounds, and total suspended particles. The NAPAP database provides a large body of information in this respect for the sources in U.S. and Canada. Similar approach is used in Europe to assess sources and fluxes of atmospheric heavy metals and persistent organic pollutants within various activities of the UN ECE Task Force on Heavy Metals Emissions and Task Force on Persistent Organic Pollutants, as well as within PARCOM and HELCOM.

Several parameters affect the accuracy of emission data prepared using emission factors. The emission factors need to be representative for a given source category, sub-category, and industrial activity. Therefore, the quality of emission data are dependent upon selection and utilization of emission factors which are transparent with respect to the conditions, both technical

and meteorological, at the time the factors were determined. Various sets of emission factors were used to calculate emission quantities for the study area by EPA and the Canadian authorities. Emission factors used in the preliminary version of the EPA emission inventory for heavy metals in the United States (Benjey and Coventry, 1992) seem to overestimate the emissions of mercury, arsenic, cadmium, and particularly lead. They are higher than the emission factors used in Canada (Voldner and Smith, 1989; Johnson *et al.*, 1990) and Europe (Axenfeld *et al.*, 1992; Pacyna, 1986). The preliminary EPA emission factors are now being revised. They need to be validated and cross-checked. For example, methods proposed recently within the UN ECE Task Force on Emission Inventories could be used for verification of emission data for heavy metals and persistent organic compounds (Mobley, 1992).

In summary, the process of collecting information on emissions for heavy metals and persistent organic pollutants from important sources in the Great Waters region has begun. However, it will take some time before an accurate emission inventory becomes available. This conclusion is made on the basis of the existing data for the region and research plans, including those within the international organizations dealing with the emission inventorying for atmospheric heavy metals and persistent organic compounds. Therefore, the analyses and particularly conclusions based on presently available emission data for the study region should be considered with some caution. This situation is similar in Europe in terms of atmospheric input of heavy metals and persistent organic compounds to the North Sea and the Baltic Sea. The overall conclusion from the research in Europe is that the current state of knowledge on emission fluxes of the above pollutants needs further improvement in order to satisfy requirements posed by policy makers and the scientific community.

#### **4.5. Application of source-receptor techniques to study the origin of pollution**

Although the source apportionment techniques are most widely used to assess the sources of air contamination at distant locations, chemical mass balance model can be applied to identify contributions from local sources, such as in an urban area (Scheff and Wadden, 1991). There have been attempts to construct both static and dynamic mass balances for various pollutants in the study area in order to quantitatively account for the pollutant loadings and the flows through the environmental system. The mass balancing method has been applied in the Great Lakes basin to manage phosphorus load reductions to Lake Erie, and to elucidate behavior in smaller regions, such as Saginaw Bay, as reported by Mackay (1992) for the Virtual Elimination Task Force.

The current level of knowledge of loadings, water and sediment concentrations, and biota concentrations is not satisfactory and several assumptions need to be made when preparing the

chemical mass balance for the study area. We are also limited by the available knowledge on the behavior of pollutants in the environment. The physical and chemical processes that are important depends upon the pollutant being investigated, and varies drastically from organics to metals, and even more for mercury.

## 5. IDENTIFICATION OF DISTANT SOURCES

Atmospheric deposition has been identified as one of the major, if not dominant, pathways for toxic heavy metals and persistent organic pollutants measured in the Great waters. However, there is no definitive information available to the authors of this report which indicates the relative contributions from local and distant sources. There is presently a limited amount of information on the transport and deposition of HAPs to the Great Lakes (Rice *et al.*, 1986; Voldner and Schroeder, 1990) which originated outside the Great Lakes Basin. However, there has recently been a number of studies which investigated the long-range transport and deposition of organochlorines (OCs) to remote areas such as the Arctic. Regional transport of metals, including mercury, and other toxic compounds is also the subject of intensive studies at EPA at present (e.g. Clark, 1992). While this compelling evidence gives indirect proof that this phenomenon is important to the Great Waters, there is still a lack of quality data on the hazardous pollutants to support a definitive conclusion. However, the results from two research programs: National Acid Precipitation Assessment Program (NAPAP) and the Baltic Sea Environmental Program in Europe can provide clues on the potential contribution of distant source emissions to the atmospheric deposition in the Great waters region.

NAPAP focused mainly on the deposition of acidic compounds and their precursors. The atmospheric transport and deposition of sulfur is discussed here as an example for the transport and source-receptor relationships for pollutants that undergo chemical transformation and that are on particles including heavy metals and persistent organic pollutants. The transport and chemical transformations for organics and metals, such as mercury, may be quite different and direct analogies should not be drawn at this time. NAPAP (1990) concluded that for receptors in the eastern United States, more than 70% of the total deposition of sulfur originates from sources within 500 km of the receptors and dry deposition of sulfur species contributes more than half to the total deposition at the average receptor. In Canada, about two-thirds of the total deposition at average receptors originate from source areas at distances greater than 500 km from the receptors. Wet deposition constitutes about two-thirds of the total deposition (except receptors close to large point sources of sulfur emissions). As the main sources of heavy metals and persistent organic compounds are south of the Great Lakes Basin and these pollutants are more



resistant to wet deposition, one can hypothesize that emissions from regions outside the Great Waters are very important when performing source apportionment studies for the Great Waters. While the evidence to date strongly suggests that distant sources are contributing to the contamination of the Great Lakes and other bodies, further research is needed to prove this hypothesis and to quantify the relative loadings for specific pollutants.

There has been a great deal of work looking at similar problems facing large bodies of water in Europe. The Baltic Sea and the Great Waters can be compared taking into account similarities in the level of water contamination by heavy metals and persistent organic pollutants, and emission source categories contributing to this contamination, although the meteorological conditions, and particularly precipitation patterns are quite different. The Baltic Sea Program concluded that major source regions contributing to the atmospheric deposition of heavy metals and persistent organic compounds except for pesticides are located several hundred kilometers from the Baltic Sea shore (Pacyna, 1992). Most of the major contributing point sources identified within the study were at least 500 km far from the Baltic shore. Even so, emissions from these sources and source regions were found to contribute the majority of the pollution load from the atmosphere. The above results confirm that the regions with high emissions of toxic metals and organic compounds can contribute to the contamination of the environment at remote receptors.

When diagnosing the major sources of contaminants in the Great Lakes Basin, for example, the large emissions of arsenic, cadmium, lead, mercury, and other heavy metals in Missouri (Benjey and Coventry, 1992) can be transported and deposited in the basin. Data supporting the transport of toxic compounds from the St. Louis area to Lake Michigan were obtained during the Lake Michigan Urban Air Toxics Study performed during the summer of 1991. The largest air pollution episode observed during the study was associated with mixed-layer transport from the general area around St. Louis, MO to the southern Lake Michigan area (Keeler *et al.*, 1992). Measurements of all of the toxic air pollutants discussed in this report were made at several sites around Lake Michigan. Preliminary results suggest that the iron-steel and other metallurgical activities in the St. Louis/Granite City area were probably the largest sources of heavy metals measured in Chicago and South Haven, MI. Additional research is needed to further support this hypothesis both with further measurement and through the application of long range transport models. The major difficulty in applying dispersion models to this problem is obtaining a set of reliable emission data within the specified grid system.

### **5.1. Emissions from North America outside the Great Waters Regions.**

Contribution of heavy metals and persistent organic pollutants from North American sources located outside the Great waters study regions can be assessed with the help of source-receptor techniques. However, the results would indicate contribution of either emissions generated within major source categories or arriving from major source regions if the source - receptor techniques are used together with information on meteorological conditions. Emission data for major point and area sources within the U.S. and Canada are needed in order to verify the results of source-receptor techniques and can be used for developing strategies to reduce the pollution load to the Great waters. The preliminary results from the EPA and the IJC data (e.g. Voldner and Smith, 1989) indicate that four states lead the emissions of heavy metals generated from the production of energy and industrial goods. The states include: Arizona, Louisiana, Missouri, and Texas. Primary copper smelters in Arizona result in high emissions of arsenic, mercury, and cadmium. Secondary smelters, refineries, and lead alkyl plants emit large quantities of lead in Texas and Louisiana. Combustion of fossil fuels, and primarily coal in Missouri, produce large amounts of all studied heavy metals. Industrial activities in Nevada, Montana, Utah and New Mexico also generate substantial amounts of atmospheric heavy metals. Recent EPA study on toxics in the community (1990) listed a ranking of states emitting toxic pollutants to the air in 1988. The list was topped with Texas followed by Ohio, Tennessee, Louisiana, Virginia, and Utah. The list of the top ten was completed by the states in the study area: Indiana, Illinois, Michigan, and New York. Quebec and Manitoba in addition to Ontario generate the largest amounts of studied heavy metals in Canada (e.g. Voldner and Smith, 1989).

Primary emission sources of PAHs to the atmosphere include combustion of fuels for heat and power generation, transportation, solid waste incineration, industrial processes such as coal and coke processing and petroleum refining. Therefore, their sources are similar to the sources of mercury (except transportation) and the states of Missouri, Texas, and Louisiana generate the largest PAH emissions.

The ubiquitous past use of PCBs as well as current generation led to widespread geographical distribution of these pollutants in U.S. and Canada. The leaks and spills from current use all-over U.S. and Canada appear to be the largest source of PCBs to the environment.

The major primary sources of PCDDs and PCDFs to the atmosphere include the combustion of municipal and industrial waste in many locations in U.S. and Canada. Therefore, the emissions of these pollutants are quite ubiquitous. In addition, it has been speculated that the dominant sources of PCDDs to the total environment could be manufacturing of chlorophenols

and their derivatives and the disposal of chemicals containing these wastes (e.g. Voldner and Smith, 1989). Although the locations of the companies which have been major producers and formulators of these products is known, no data is available to speculate on the likely emission amounts.

Information on the use of lindane in U.S. and Canada is very limited. Its application in agriculture is banned but is probably used in livestock treatment. The use pattern of lindane in U.S. and Canada is largely unknown.

It is postulated that large sources of atmospheric emissions of heavy metals and persistent organic pollutants are located in Mexico, and that the effects of these sources are being felt in Great Waters areas (Eisenreich and Strachan, 1988). Two attempts have been made within the Global Emission Inventory Activities (GEIA) program of the International Geosphere Biosphere Program (IGBP) to assess the sulfur dioxide and nitrogen oxides emissions in Mexico as a part of the global emission inventory for these pollutants. The assessment has been made in co-operation with the Mexican experts and it was concluded that the sulfur and nitrogen emissions divided by the number of inhabitants was one of the largest in the world. As the combustion of fossil fuels is by far the most important source of sulfur emissions, it can be expected that substantial amounts of mercury are also emitted into the atmosphere from the Mexican power plants, particularly due to the lack of desulfurization installations on these Mexican plants.

Large quantities of nitrogen oxides are emitted in Mexico from the combustion of gasoline. The Mexican gasoline contains lead in amounts of 0.4 g/liter and results in emissions to the atmosphere which are also relatively high. Recently, a preliminary study was been carried out at the Norwegian Institute for Air Research to assess global emissions of atmospheric lead. The study is a continuation of global emission inventory development for which preliminary results have been published by Nriagu and Pacyna (1988). It has been estimated that at least 5000 t of lead is emitted from gasoline combustion in Mexico each year, compared to about 15000 t in U.S. in 1985. Current emissions of lead in U.S. are significantly lower than those in 1985 and probably do not exceed 7000 t per year.

Mexico is also an important producer of non-ferrous metals and particularly copper, lead, zinc, cadmium, arsenic, silver, gold, antimony, and bismuth. There are several companies in the country producing the above metals with the two major ones being Industrial Minera Mexico SA de CV, and Industrias Penoles SA de CV. Substantial amounts of atmospheric emissions of all heavy metals of concern for this report are expected from the concentrating facilities in Santa Eulalia (Chih.), Taxco (Gro.), Rosario (Sin.), Velardena (Dgo.), Santa Barbara (Chih.), and

smelters and refineries in Nueva Rosita (Coah.), San Luis Potosi (SLP), Chihuahua (Chih.), Monterey (NL), and Torreon (Coah). In addition, there are several secondary non-ferrous metal plants in the country generating atmospheric emissions of heavy metals. Although quantitative information was not available to the authors of this report, knowledge on industrial technologies employed in the above facilities and information on emission control equipment, although very limited, indicates that emissions from Mexican non-ferrous metal industry are higher than those in U.S..

There are several aluminum plants in Mexico operated by major companies such as Almexa Aluminio SA de CV, Aluminio SA de CV, Laminadora de Aluminio SA de CV - Lasa, and Reynolds Aluminio SA. It is expected that substantial emissions of PAHs are generated in these plants, particularly in smelters employing the Soderberg process to produce aluminum, such as the Aluminio SA de CV smelter in Veracruz. An emission factor ranging from 500 to 5000 g PAH / ton of Al produced was estimated for this process (e.g. Axenfeld *et al.*, 1992).

The emissions from the above described sources in North America but outside the study region can be transported and deposited to the Great Waters areas. One of the methods utilized to study the long range transport of heavy metals and organic pollutants are regional transport models. There are two major groups of input data needed to employ these models: gridded emissions data and meteorological input data including wind and precipitation observations from surface and upper air meteorological sites. The emissions data are always more difficult to obtain and as such they should be given a priority in future research plans. This task requires not only a financial support but also international co-operation.

## **5.2. Emissions from sources outside of North America.**

Measurements in the Great waters region show presence of pollutants which are banned in U.S. and Canada entirely or partially. One of this pollutants is  $\gamma$ -hexachlorocyclohexane, an insecticide called lindane. An interesting question is what may be the origin of lindane measured in regions where its use is banned.

There is rather limited information on the use of lindane in the literature although this pesticide is widely used in various parts of the world. The Food and Agriculture Organization (FAO) statistics indicate that large amounts of lindane have been used by several countries during the last two decades, particularly in Asia. Although it is difficult to obtain exact values, the production and use of lindane in India and China is at a level of tens of thousand of tons per year in each of these countries (as indicated by Semb and Pacyna, 1988). Similar amounts are believed

to be used on the former Soviet Union as reported by Komarov (1980). Lindane is used in the above mentioned countries to improve the agricultural crop yield and to reduce diseases. Lindane has been also used in Europe and Australia (reported by Semb and Pacyna, 1986 after other authors).

Recent investigations of the Arctic air pollution have shown that lindane has been present in appreciable amounts in air samples collected at the ground stations as well as with the use of the aircraft (Pacyna and Oehme, 1988). The authors suggested the Asian continent as the probable source of the lindane. During the spring storms in the Asian deserts fractions of dust with small particles can become airborne and subject to long-range transport within air masses. Spring is the period with extensive use of lindane and other pesticides in Asia. Therefore, it is reasonable to suggest that lindane is taken up with dust particles and transported out of the region (Pacyna and Ottar, 1989). It is suggested here that lindane measured in the Great waters region can originate partly in Asia through the process described above. A possibility of long range transport of air pollutants from the Asian continent over Hawaii to the western United States and then further east has been already proposed to study, however no support was obtained. It should be added that our understanding of meteorological processes governing the movement of air masses and wind patterns do not exclude the possibility of the air mass transport from Asia to North America.

Of course, other source regions can not be excluded when discussing the origin of lindane in the Great Waters region, e.g. the Latin American countries. It is well established that certain organochlorine compounds, such as DDT and PCBs can be deposited to lakes far removed from their source (Hites and Eisenreich, 1987). The concentration ratio of  $\alpha$ - to  $\gamma$ -hexachlorocyclohexane (HCH) in air masses can be a helpful tool to estimate the residence time of aerosols and then to assess source regions. The  $\gamma$ -HCH is photochemically transformed to the  $\alpha$ -isomer. Pacyna and Oehme (1988) concluded that the ratios of 50 and higher would indicate old air masses. These values would be expected in the Great waters region if the HCHs were to be from the sources in Asia.

It is rather difficult to expect emissions from parts of the world other than mentioned above to contribute directly to the deposition in the study region. One theoretical possibility could be an episodic transport of pollutants with the Arctic air masses. Emissions from various source regions contribute to the contamination of Arctic air, especially from sources in northern part of the former Soviet Union and Europe - so called Eurasian sources. One of the major scientific questions still to be answered by the Arctic researchers is what happens to the pollution load entering the Arctic region. A part of this load is deposited to the surface but meteorological

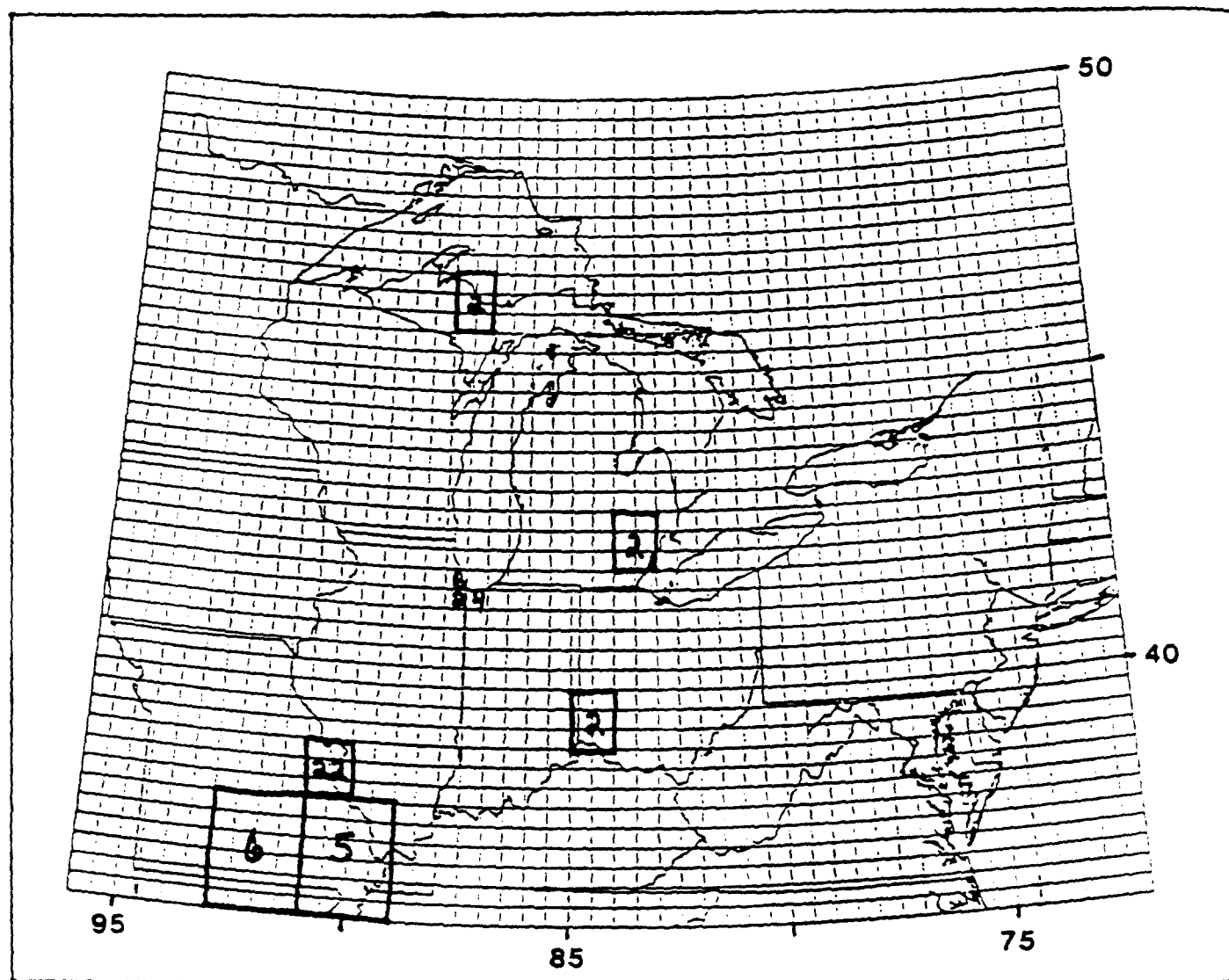
conditions in the Arctic do not favor efficient deposition of the pollutants. Thus one theory suggests that a part of the pollution brought to the Arctic is carried-out of the region (e.g. Pacyna and Shaw, 1991). Could part of this pollution load reach the Great Lakes and other Great Waters under certain meteorological conditions? If so, what is the frequency of occurrence? These questions need to be addressed in the future research activities in both the Great Waters regions and the Arctic.

### **5.3. Application of source apportionment techniques for identification of impacts of emissions on the Great Waters from distant source regions.**

There have been only a few studies to date which attempted to diagnose the sources of toxic air pollutants in the Great Lakes basin. Mamane *et al.* (1992) carried out a systematic study of the sources of pollutants and toxic compounds measured in the air over Green Bay as part of a larger study of toxics deposition to Green Bay. Their findings suggest that regional source influences were the dominant contributor to the particulate mass measured during the study. They also identified incinerator emissions impacting the measurement site as the concentrations of Cl, K, and Pb in fine particles were 2 to 3 times higher than average in these samples. Confirmation that one or more incinerators contributed to the metals measured on particles in Green Bay was found by SEM analysis of individual particles collected on the filters. However, this study did not directly quantify the sources of the pollutants deposited to Green Bay.

More recently, Clark has utilized the RELMAP model to calculate the transport and deposition. The RELMAP model is a lagrangian dispersion model which relies upon the availability of accurate emissions data for the compounds of interest. Utilizing dispersion models for defining source-receptor relationships offers the distinct advantage that one can directly calculate the contributions from various sources to the actual deposition to the lakes. The total deposition (dry + wet) of Pb to Lake Michigan was estimated by Clark (1992) and the source-receptor relationships are given in Figure 28. Cells which had sources contributing more than 2% of the total annual atmospheric deposition directly to Lake Michigan are indicated on the Figure. The preliminary modeling suggests that sources of Pb outside of the Great Lakes Basin are in fact the major contributors to the Pb deposition to Lake Michigan. Figure 29 shows the relative contributions of sources contributing to the deposition of Cd to Lake Michigan. Figure 30 shows the relative contributions of sources contributing to the deposition of benzo(a) pyrene to Lake Michigan. The relative contribution pattern for this PAH compound is quite different than those seen for Pb and Cd. The contribution of BaP is primarily from local sources in the Chicago/Gray area.

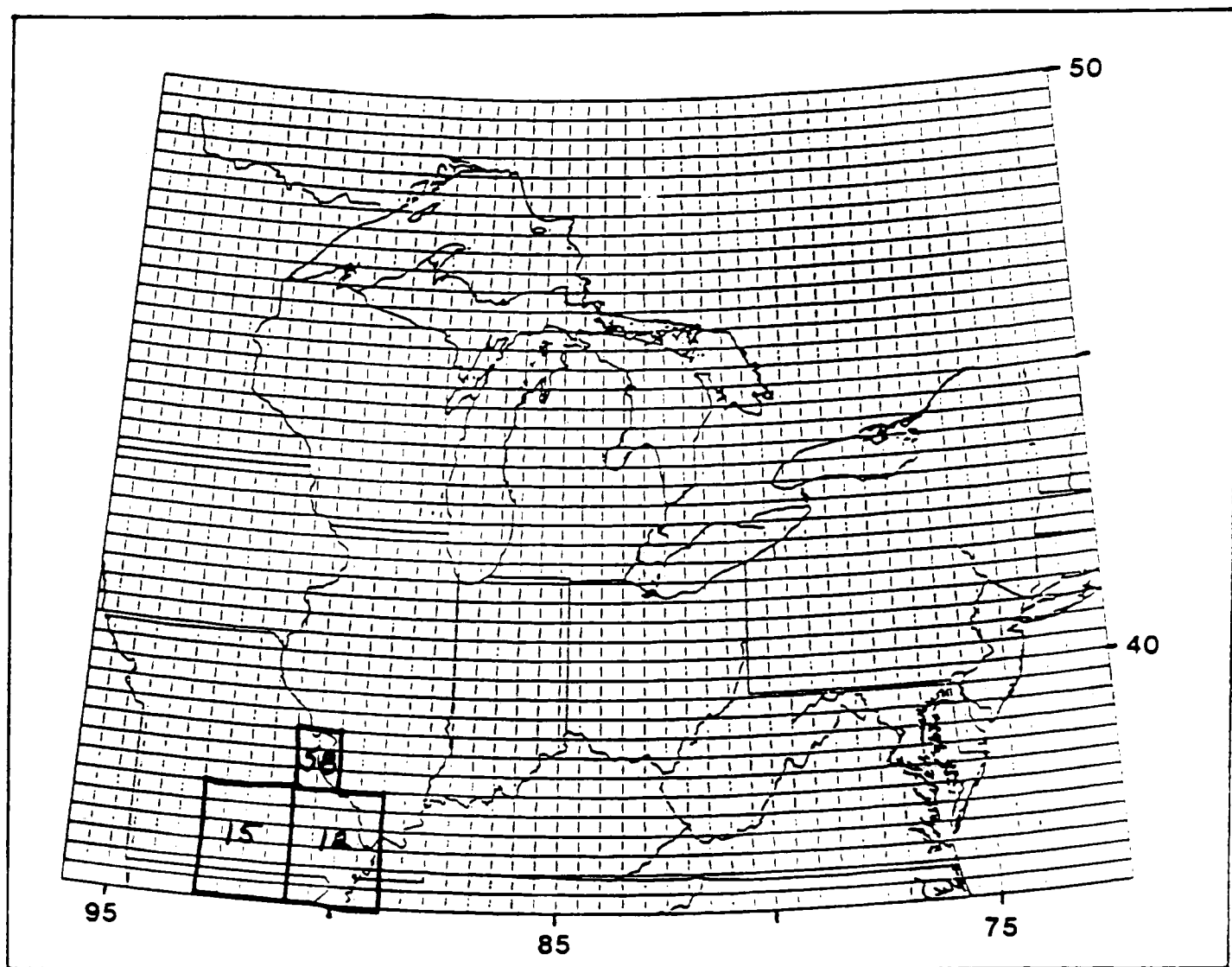
# 40-KM EMISSION/DEPOSITION GRID FOR MODELING TOXICS



## PERCENTAGE CONTRIBUTION TO LAKE MICHIGAN DEPOSITION LEAD

Figure 28. The relative contribution patterns for total annual deposition to Lake Michigan. Preliminary modeling estimates from Clarke (1992).

## 40-KM EMISSION/DEPOSITION GRID FOR MODELING TOXICS

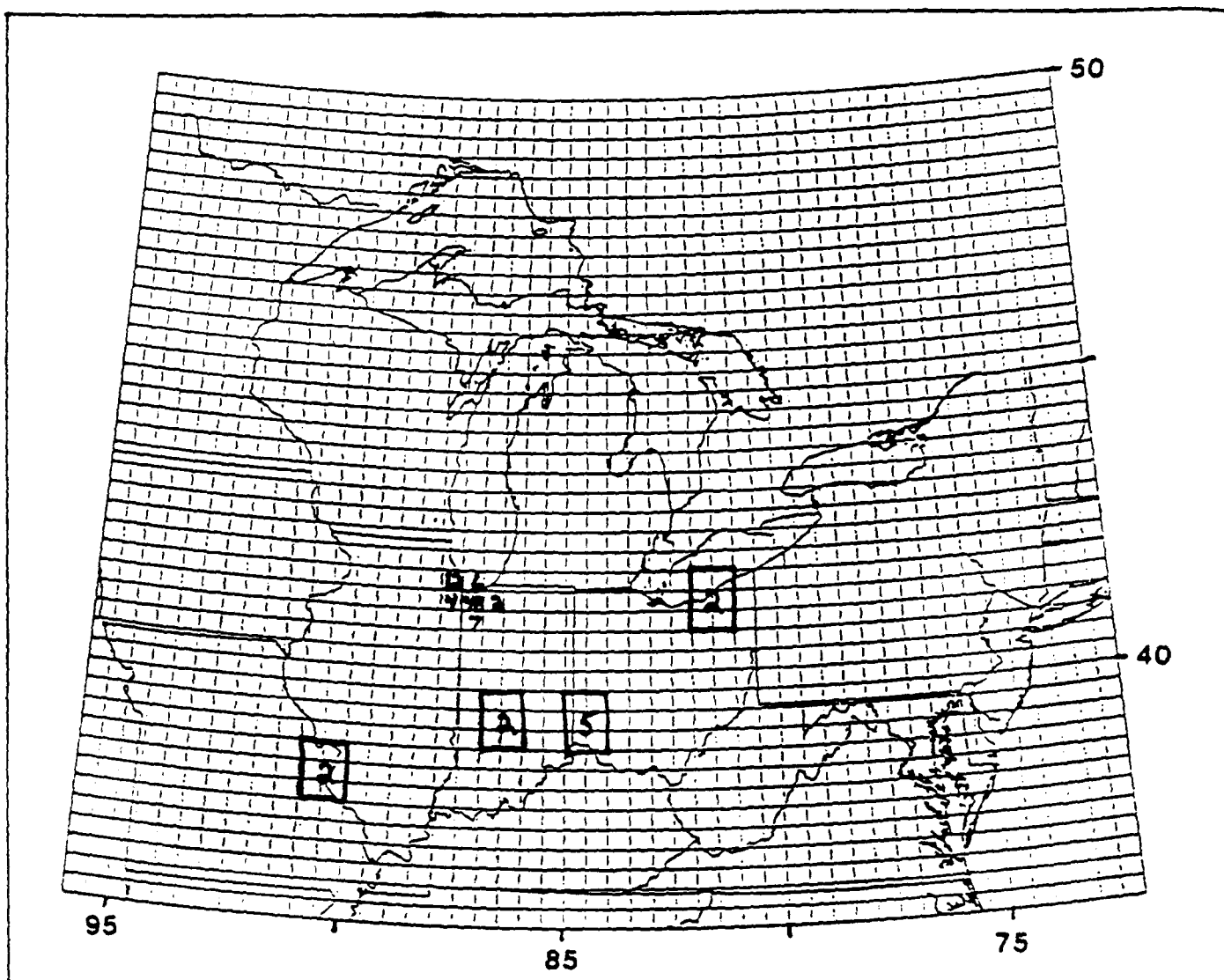


## PERCENTAGE CONTRIBUTION TO LAKE MICHIGAN DEPOSITION CADMIUM

Figure 29. The relative contribution patterns for total annual deposition to Lake Michigan. Preliminary modeling estimates from Clarke (1992).



40-KM EMISSION/DEPOSITION GRID FOR MODELING TOXICS



PERCENTAGE CONTRIBUTION TO LAKE MICHIGAN DEPOSITION  
BENZO(A)PYRENE

Figure 30. The relative contribution patterns for total annual deposition to Lake Michigan. Preliminary modeling estimates from Clarke (1992).

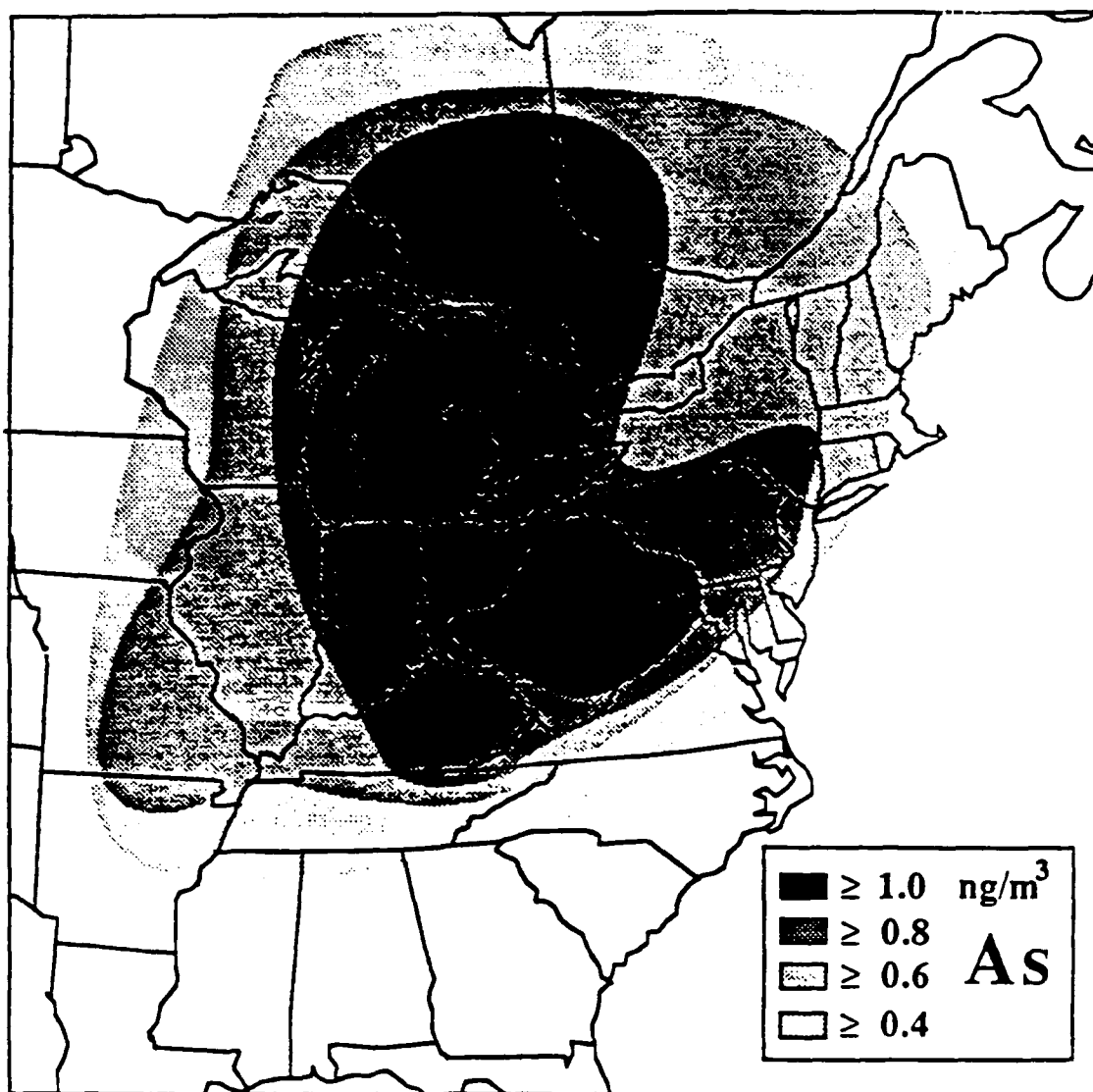
Rahn *et al.* (1989) applied their regional signature technique to the aerosols and precipitation samples collected in Underhill Vermont. They estimated that approximately 80% of the sulfate and selenium originated from sources located in the Midwest whereas 20% of the sulfate and selenium deposited to the Lake Champlain basin were derived from local sources on the East Coast. Keeler and Samson (1989) applied a hybrid receptor model to investigate the utility of using the "regional signature" approach and concluded that variations in elemental ratios may reflect different mixes in emissions of sources in different source regions. In their analysis Keeler and Samson calculated the source contribution fields using Quantitative Transport Bias Analysis (Keeler, 1987) for several heavy metals including arsenic measured in the eastern North America. The contribution field for As contributions is given in Figure 31. This analysis would suggest that the largest contributor to As concentrations measured during the month of August, in the Lake Champlain basin for example, was found in the Midwest area around Pittsburgh but that significant contributions were also observed from a large region extending up towards the Canadian smelters in Sudbury and Noranda.

## **6. BENEFITS FROM EMISSION REDUCTION**

A number of the abatement techniques are available for the reduction of emissions of pollutants studied in this work and emitted from sources in the Great Waters area. Implementation of these techniques shall result in several benefits which can be measured in a local environment, e.g. around a given point source of emission, as well as in the whole region of the Great Waters.

Various alternatives to reduce emissions apply to anthropogenic sources. Emissions from natural sources are very difficult to control, if impossible. In general, different alternatives are proposed for stationary (point) and mobile sources. It is not intended here to discuss the applicability of different alternatives to reduce emissions or even their detailed description. It is, however, important to identify various alternatives in a view of benefits resulting from their implementation.

Three different groups of methods can be identified for reductions of emissions from variety of point sources: application of best available technology (so-called BAT, or best practicable technology - BPT), methods leading to increased energy efficiency, and methods resulting in waste minimization. The BAT concept is based on the application of the state-of-the-art control technology to remove pollutants from exhaust gases. As a majority of heavy metals and persistent organic pollutants from industrial sources is released on particles, the BAT in this case is concerned with the equipment to efficiently remove dust from exhaust gases leaving primary and secondary iron and steel plants, primary and secondary non-ferrous smelters,



**Figure 31.** The spatially averaged As contribution to ambient concentrations in the northeastern United States during August, 1983.

ferroalloy plants, waste incinerators, and fossil fuel power plants producing electricity and heat. In general, the installation of fabric filters or equally efficient control techniques (e.g. electrostatic precipitators - ESPs) with practical removal efficiency of better than 98% for fine particles (with diameter smaller than  $2\ \mu\text{m}$ ) will assure the reduction of dust concentrations in the exhaust gases lower than  $10\ \text{mg}/\text{Nm}^3$ . It should be admitted that both, primary exhaust gas and fugitive emissions must be controlled. The installation of BAT as described above will result in reduction of up to 95% of heavy metals and persistent organic pollutants on particles, introduced to the industrial processes as impurities of raw materials (Pacyna, 1992).

Removal of mercury from exhaust gases is different than the removal of other heavy metals, as the majority of the mercury emissions occurs in a gaseous phase. Therefore, BAT for mercury removal includes both wet scrubbers and ESPs, capable of reducing metal concentrations in exhaust gases to at least  $50\ \mu\text{g}/\text{Nm}^3$ . A presence of any flue gas desulfurization technique results in removal of 40 to 80% of gaseous mercury in exhaust gases.

Removal of dioxins from exhaust gases of waste incinerators could be obtained through the application of various flue gas cleaning techniques. The dry flue gas cleaning with scrubbing on fabric filters has proved to be very efficient to remove dioxins on an industrial scale in waste incineration plants.

Reduction of emissions of heavy metals and persistent organic pollutants can also be obtained through application of so-called pre-treatment methods, and first of all washing of raw materials before use and switch of fuels. In fact both methods are applied primarily to fuels and not to other raw materials. It has been recently concluded that washing of coal prior to combustion results in removal of 10 to 30% of heavy metals contained in coal (reported by Pacyna, 1992). Fuel switching can be used in some operations which involves replacing some of the coal and residual oil fired in a boiler with select natural gas. The degree of emission reduction depends on the amount of fuel to be substituted and the kind of fuel. In the best cases up to 80% reduction can be obtained.

Appropriate design and management of the combustion processes in new incinerators would result in considerable reductions in dioxin formation when compared with many existing incinerators and could bring the emission back to about  $1\ \text{ng TEQ (Toxic Equivalents Quantity)}/\text{Nm}^3$ .

Reduction of emissions through the application of techniques leading to increase of energy efficiency is based on the use of so-called primary reduction measures. An example of such

measures is modification of combustion processes leading to higher combustion efficiency (through suitable manipulation of the stoichiometry/temperature profiles within the boiler). It is difficult to assess to what extent the emission reduction can be achieved through the combustion modification. For gaseous pollutants, such as nitrogen oxides a reduction range of 60 to 90% was found technically possibly (reported by Pacyna, 1992).

Emission reductions can also be obtained through minimization of wastes. Production technologies resulting in lower amounts of exhaust gases should be given priority over the technologies with large quantities of waste gases. The cost of emission control installations is usually lower for the low waste gas technologies to produce a certain industrial product.

The use of unleaded gasoline is the best option to reduce lead emissions from mobile sources. Extended research has been carried out on the cost and benefits from using the unleaded gasoline (e.g. CONCAWE, 1980; CEC, 1984). A production of unleaded gasoline requires about 5% increase in total energy (crude oil). A considerable reduction of dioxin input to the atmosphere from vehicles can be achieved through the general use of catalytic converters and the use of unleaded gasoline.

Reduction of emissions of pollutants in the Great Waters Study areas may be achieved through decreases in vehicle miles traveled, fuel reformulation, as well as through the introduction of alternative vehicles. Tailpipe controls result in lowering emissions from other area sources.

There are also alternatives to reduce emissions from fugitive and indirect sources although control of releases from these sources is much more difficult than the control of emissions from the above discussed sources. Landfills should be organized as controlled landfills connected to waste water treatment plants if possible. Leaching potential of metals, defined as the fraction of metal present in a solid waste that may become water - soluble under certain chemical conditions should be controlled at least for volatile metals, such as mercury.

The phasing out the pesticides which are the most persistent, toxic and liable to bioaccumulate is the best way to deal with the unwanted environmental effects of these chemicals.

The implementation of the emission reduction techniques as described above would improve the quality of the environment through the reduction of atmospheric deposition of the pollutants of interest. This is the major environmental benefit. The reduction of atmospheric deposition will inevitably decrease the uptake of pollutants by surface waters, soils, and plants in the vicinity of major point sources of emissions, and limit migration of these pollutants through various environmental media.

Installation of equipment to reduce the dust concentration in exhaust gases, or improvement of its performance will contribute to the improvement of air visibility in the study region.

Reduction of atmospheric emissions of heavy metals and persistent organic pollutants will result in lowering their intake to human body, mostly due to reducing their ingestion in the study region. This intake has already exceeded the WHO/FAO maximum permissible values for some pollutants in some locations within the study area.

Implementation of emission control techniques will be a substantial step towards improving the chemical and to some extent biological recovery of the environment in the study area. As a result, an increase of fish population, an important factor of local economy in the region, can be expected. The most obvious and measurable costs are those that stem from damage to fish and wildlife and the loss of commercial fisheries represents one of the first and most easily identifiable losses of economic value. As indicated in the documents for virtually eliminating inputs to the Great Lakes, loss income estimates, in 1990 dollars, due to toxics-related closures or market losses could be as high as 8.5 million dollars per year including only losses due to mercury in Lake St. Clair and toxics in Lake Ontario. Since most of the emissions deposited in the study region originate outside the region, limitations of these emissions will reduce deposition in a much larger region than the study area.

## **7. CONCLUSIONS**

1. Atmospheric deposition is one of the major sources of lead, arsenic, cadmium, mercury, PAHs, lindane, and possible PCBs, PCDDs, and PCDFs measured in the Great Waters. The other sources include leaching from the landfills, direct industrial discharges, agriculture practices in the region, transport with river waters, and direct dumping of wastes. However, identifying the specific sources or source types emitting the pollutants into the atmosphere which ultimately are deposited is another matter. Identification of the dominant pathway and the major sources of the critical pollutants should be made for the individual compounds separately as their sources and behavior in the environment differ substantially.
2. Emissions from sources within and outside the Great Waters regions both contribute to the load of pollution in atmospheric deposition to the waters in the region. Although a number of source-receptor techniques are available for estimating the contributions, it is still premature to conclude what part of pollution load originates within the study region and what part results from long range transport within air masses. The major reason for the present uncertainty is the lack of

reliable input data for application of these techniques including properly reported emission data. The present lack of monitoring data as well as emissions information is also problematic for other regions, e.g. the North Sea and the Baltic Sea, the two most extensively studied regions in Europe with respect to the environmental behavior of toxic heavy metals and persistent organic pollutants.

3. Identification of emission sources in the Great Waters regions and their characterization with respect to atmospheric emissions has been carried out for some time in both the United States and Canada. As a result, major source categories have been defined for all of the studied pollutants. The major sources include: production of electricity and heat, combustion of fuels in industrial, commercial, and residential units, including wood combustion, manufacturing and use of various industrial goods, and incineration of municipal and industrial wastes, and incineration of sewage sludge dominate in the group of local sources. There are, however, differences in quantitative assessment of the fluxes from the above sources, reported by various research groups in the United States and Canada. These differences should be resolved through thorough examination of the available data using various techniques of verification of emission data and joint supplementary research programs in both countries.

4. Emissions from other source regions in North America may also affect the amount of pollution load deposited to the Great Waters although no evidence has been provided by measurements and assessment for heavy metals and persistent organic pollutants. The NAPAP concluded that such an impact exists for deposition of sulfates. As the sulfates are transported within air masses on particles, as so do most of the metals and organic compounds discussed in this report, one would also hypothesize that the metals and organic compounds emitted from sources outside the study region can be deposited to the Great Waters. At present, regional models of long range transport of air pollutants are available and with some modifications they can be used to assess the contribution of emissions from outside source regions to the Great waters. An emission inventory with the appropriate spatial distribution of the data needs to be prepared. The experience gained through NAPAP emissions inventory development can be used as a starting point for this purpose. Collaboration with the Mexican authorities on environment protection is highly recommended as the Mexican emissions of heavy metals and persistent organic pollutants are expected to contribute to the contamination of the Great Waters.

5. Lindane was found to be a global air pollutant measured in remote areas around the world. As the major application of this pesticide is in Asia and the wind patterns at various altitudes do not exclude the air mass transport from the Asian continent to North America, lindane deposited in the Great Waters regions may originate from as far away as India, China, or the former Soviet

Union. This hypothesis can be tested by the application of global models, or at least hemispheric models. At present, such models are used to study the transport of green-house gases in the atmosphere and the transport of sulfur in the Northern Hemisphere. A knowledge of emission rates or fluxes of lindane in Asia within 1 degree by 1 degree grid system should be elaborated for the use in the models. This task can be carried out in co-operation with international programs involved in preparation of global emission inventories, e.g. the IGBP program on Global Emission Inventories Activity (GEIA) or the OECD program on emission of greenhouse gases.

6. Several methods can be applied to reduce emissions of toxic heavy metals and persistent organic pollutants and eventually reduce the atmospheric deposition of these pollutants to the Great Waters. Technological solutions presented in a form of Best Available Technology (BAT) package or Best Practicable Technology (BPT) package offer emission reduction possibilities for point sources within all major source categories contributing to the contamination on the Great Waters. Experience gained in this respect in North America and Europe, and particularly in the Baltic Sea Environmental Program can be useful in recommending emission reduction scenarios in the Great waters region. Cost estimates and benefits from the implementation of the control techniques should be carefully studied. Experience gained during NAPAP may prove very useful.

## **8. RECOMMENDATIONS ON FUTURE RESEARCH ACTIVITY TO IMPROVE THE ACCURACY OF METHODS FOR SOURCE IDENTIFICATION**

New research initiatives are necessary in order to meet the requirements outlined in the conclusions of this report as well as to test the important hypotheses proposed here. These activities would include both measurement programs and modeling estimates.

### **8.1. Measurement programs**

New measurement programs are needed in order to improve the quality of source-receptor techniques which are used to assess the magnitude and origin of deposited pollutants. These measurements are needed at both the receptor, the Great Waters themselves, as well as at the sources of the emissions. The following source emissions information are recommended:

- emission rates and emission factors for toxic heavy metals and persistent organic pollutants from large point sources in the study region should be evaluated on the basis of measurements of their concentrations in exhaust gases. Large point sources should include electricity and heat producing plants, ferrous and non-ferrous metal smelters, cement kilns, and waste incinerators.



They can be defined as in the CEC directives. The emission measurements shall be representative and their reporting transparent;

- physical and chemical forms of the most volatile compounds should be established through measurements carried out in major sources in the study area; and
- emission rates for the most volatile metals, and particularly mercury, as well as lindane and other pesticides should be derived on the basis of measurements over the water surface in the Great Waters and the surrounding soils. The results should be representative for the meteorological conditions as in the Great Waters and exemplify seasonal changes.

Measurements at receptors should provide with the information which is needed in order to improve the accuracy of source-receptor relationship analysis. The following is recommended:

- size-differentiated chemical composition of aerosols should be measured at receptors which can represent conditions over the water surface in the study area. The results used in various statistical methods for source-receptor modeling, e.g. principal component analysis can be used to improve the accuracy of identification of source categories discussed; and
- simultaneous measurements of the gaseous and particle phases of the studied pollutants with the help of newly developed techniques (e.g. denuder methods) should be undertaken in order to provide information on gas-to-particle conversions ( and particle-to-gas conversions) for the most volatile pollutants under study. The results should be useful to explain the chemical behavior of these pollutants, particularly during the episodes of their transport within air masses from source regions to the receptors in the Great Waters areas.

## **8.2. Modeling estimates**

Improvement is needed within the three groups of estimates: emission estimates, dispersion modeling, and receptor modeling.

The following is recommended for the improvement of emission estimates in order to assure better understanding of source identification in the Great waters region:

- a set of emission factors and emission rates should be prepared for all sources contributing to the contamination of the Great waters, and particularly for sources or even whole source categories for which measurements are not available. In general, rather limited information exists on emission factors for heavy metals and even less for persistent organic compounds. In the past

major research has been carried out in Europe, particularly within the UN ECE programs, PARCOM, and HELCOM. Recently several projects have been carried out in North America, mainly for EPA, IJC, Ontario Ministry of the Environment, and Environment Canada. The information on emission factors, available from the above mentioned programs should be reviewed and a set of emission factors and emission rates selected with the aim of their application to prepare emission inventory for atmospheric heavy metals and persistent organic compounds in North America with special emphasis on the sources within the Great waters region. Guidelines on emission estimation and reporting should be elaborated in order to assure the data representativeness, comparability, completeness, consistency, and accuracy. As the subject is of broad interest, a close co-operation with other programs and international organizations is highly recommended, particularly with the UN ECE task forces on emission of heavy metals and persistent organic pollutants;

- gridded emission inventory for the studied pollutants should be approached for the whole territory of the United States and Canada. A large body of information on the parameters used to prepare spatial distribution of emission data, e.g. geographical location of point sources and surrogate parameters to distribute emissions from area sources has been collected during NAPAP. This information should be used to distribute the emission data for pollutants under study here;
- seasonal changes of mercury and volatile organic compound emissions need to be quantified and techniques developed to estimate these emissions; and
- an approach should be defined to assess emissions of pesticides (e.g. lindane) in the Northern Hemisphere with particular emphasis on Mexico and the Asian countries. This task should be carried out in co-operation with international organizations, such as IGBP

Improvements in source identification through the further development of dispersion modeling is needed. The following are recommended:

- continue to modify and improve the existing long-range transport models so they can be used to study the contribution of emissions from sources in North America, both within and outside the study region to the hazardous pollution load deposited to the Great Waters. Models developed during NAPAP as well as in other programs in North America and Europe ( e.g. the UN ECE EMEP model) should be taken into account; and
- an approach should be made to apply the existing global scale models to investigate the possibility of lindane used in Asia to be transported within air masses to North America and deposited also in the Great Waters region.

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